# INVESTIGATIONS

ON THE

# MOLECULAR SCATTERING OF LIGHT

BY

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BEING A THESIS TOGETHER WITH OTHER SUPPLEMENTARY PAPERS WHICH WERE SUBMITTED AND APPROVED FOR THE DEGREE OF DOCTOR OF SCIENCE OF THE UNIVERSITY OF MADRAS
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WITH FEELINGS OF LOVE AND ESTEEM

TO

PROFESSOR C. V. RAMAN

# PREFACE.

THE main thesis consists of eight parts. Of these, parts 1, 2, 3, 4 and 5 describe experimental and theoretical work carried out independently by the author, partly while at Calcutta as a research student and partly at the University College, Rangoon. Parts 7 and 8 which are purely theoretical are joint productions. The experimental determinations of the scattering of light in carbon dioxide described in part 6 which forms a comprehensive test of the theory was carried out by the author personally in the course of a vacation spent at Calcutta.

Two supplementary papers are also offered.

Since the thesis was submitted to the University for the doctorate, all the papers contained herein have appeared in scientific journals. Due acknowledgments have been made at the head of each paper.

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# INVESTIGATIONS ON THE MOLECULAR SCATTERING OF LIGHT.

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## ELECTRO-MAGNETIC THEORY OF THE SCATTERING OF LIGHT IN FLUIDS.

BY K. R. RAMANATHAN.

Office of the Registrar of Books, Madras

CONTENTS.

1. Introduction.
2. Continuous Medium Theory.
3. Scattering by Isotropic Molecules.
4. Scattering by Anisotropic Molecules.
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### 1. *Introduction.*

The subject of "Molecular Scattering of Light" whose foundations were laid by the late Lord Rayleigh, gained a new significance from the experimental work of Cabannes[1] and the present Lord Rayleigh[2] on the scattering of light in dust-free gases. Its importance was further increased by Prof. Raman's[3] application of Einstein's investigation of critical opalescence to the case of scattering in fluids in general, and his explanation of the blue of the sea as being caused by molecular scattering of light in water. Experimental work by the present author[4] on the scattering of light in ether and by Mr. R. Venkateswaran[5] in normal pentane showed that throughout the range of temperatures from 35° C. to the critical point, both in the saturated vapour state and in the liquid state in equilibrium with the vapour, the intensity of scattering in a transverse direction is given by the Einstein-Smoluchowski expression (with a correction for admixture with unpolarised light).

$$I=\frac{\pi^2}{18}\frac{RT\beta}{N\lambda^4 r^2}\quad(\mu^2-1)^2\,(\mu^2+2)^2$$

where I is the intensity of the scattered light from a unit volume at a large distance $r$ from the volume.

R, N are the gas constant and the number of molecules respectively per gram-molecule

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1 Cabannes—Ann. Physique, Tome XV, 1920, pp. 1-150.

2 Rayleigh—Proc. Roy. Soc. A, 1918, p. 453.

3 C. V. Raman—Proc. Roy. Soc. A, April, 1922, p. 65 and 'Molecular Diffraction of Light,' Calcutta University Press, 1922.

4 K. R. Ramanathan—Proc. Roy. Soc. A, 1922, p. 151.

5 R. Venkateswaran—Trans. Chem. Soc., 1922, Vol. 121, p. 2655.

T is the absolute temperature
$\beta$ is the isothermal compressibility of the medium
$\mu$ is its refractive index and
$\lambda$ is the wave-length of the incident light.

The above expression was derived by Einstein on the assumption that the scattering of light was caused by the local changes in dielectric displacement consequent upon the local fluctuations of density to which an otherwise uniform medium is subject owing to the thermal movements of its parts. In such a case, the light scattered in a direction transverse to the primary beam should be completely polarised. The same result may be deduced when the individual molecules are regarded as sources of scattered radiation provided that they are supposed to be spherically symmetrical and their restricted freedom of movement is taken into account. Actually, however, the transversely scattered light is in general found to be imperfectly polarised, much more so in a liquid than in its vapour. The imperfect polarisation in gases has been explained by the late Lord Rayleigh,[1] Born[2] and Gans[3] on the assumption of molecular anisotropy. The subject has also been studied by Sir J. J. Thomson[4] from the point of view of the electron theory. The increase of imperfection of polarisation in the liquid state is remarkable and an explanation of it has been given by Raman on the idea that the scattering in a fluid can be considered to be made up of two parts, a density-scattering and an orientation-scattering of which the former is given by the Einstein-Smoluchowski formula while the latter is proportional to the density of molecules. It is obviously of importance to make an exact investigation of the connection between the state of aggregation of a medium and the quality of the scattered light, especially in view of the fact that it promises to throw light on the nature of the liquid state itself. In the following paper, an attempt is made to develop a general theory of scattering in fluids. In Article 2, the medium is assumed to be continuous as in Einstein's treatment of the subject, but subject to local fluctuations of density depending upon the laws of statistical mechanics. Lorentz's electro-magnetic treatment of the scattering of light in gases developed in his book "Les Theories Statistique en Thermodynamique" has been adopted and extended to the general case of a fluid of any compressibility. In Article 3, the subject is treated from the molecular standpoint in the case when the molecules are isotropic and the Einstein-Smoluchowski formula for scattering is deduced. In Article 4, the molecular treatment is extended to the case when the molecules are anisotropic and expressions are deduced for the intensity of the scattered light, its state of polarisation and the co-efficient of extinction in the medium. In

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[1] Rayleigh—Phil. Mag. XXX, 1918, and Scientific Paper, Vol. VI, p. 540.
[2] Born—Verh. Deutsch. Phys. Gesell., Vol. 19, p. 243, 1917, and Vol. 20, p. 16, 1918.
[3] Gans—Ann. der Physik—10, 1921.
[4] Sir J. J. Thomson—Phil. Mag. XL, 1920, p. 393.

Article 5, the results are discussed with reference to experimental data as regards polarisation of the scattered light in liquids and their vapours. Article 6 contains a synopsis of the principal results of the investigation.

## 2. "*Continuous Medium*" *Theory.*

Let $K_0$ be the value of the dielectric constant when there is a uniform distribution of matter and $K_0 + \delta K$ its actual value at a volume element $\delta v$.

In any actual fluid, owing to thermal movements, the density at any point undergoes incessant fluctuations and hence the dielectric constant also.

Using Heaviside units, the dielectric displacement

$$D = K_0 E \tag{1}$$

where E is the electric intensity. When the density and consequently the dielectric constant are uniform, there would be no scattering, for the disturbances from different elements of volume would mutually cancel each other, except in the direction of primary propagation.

At a place where the dielectric constant is $K_0 + \delta K$,

$$D_1 = (K_0 + \delta K)\,E \tag{2}$$

Here, there is a discontinuity of displacement which could be annulled by introducting a supplementary electric intensity

$$F = -\frac{\delta K}{K_0}E \tag{3}$$

For, then

$D_1$ would become $(K_0 + \delta K)\,(E - \frac{\delta K}{K_0}E)$ which is equal to $K_0E$ if we neglect $(\delta K/K_0)^2$ in comparison with unity. As matters actually are, the scattering is identical with the radiation due to a system of electric intensities $-F$ or $\frac{\delta K}{K_0}E$ at the places where the dielectric constant differs from its mean value $K_0$ by $\delta K$.

Suppose we have a volume element $\delta v$ at the origin of co-ordinates at which the dielectric constant is $K_0 + \delta K$. When the linear dimensions of the element are small in comparison with the wave-length, the amplitude of the disturbance from the element would be proportional to $\frac{\delta K}{K_0}E\delta v$ and hence its energy proportional to

$$\left(\frac{\delta K}{K_0}\right)^2 E^2 (\delta v)^2 \tag{4}$$

As a first step, then, we have to calculate the radiation caused by an extraneous periodic intensity acting throughout a volume element $\delta v$ at a given point in a homogeneous isotropic dielectric. The problem is analogous to that solved by Hertz in the case of the vibrating electric doublet.

Let E represent the electric intensity
H the magnetic intensity
D the dielectric displacement
and F the extraneous electric intensity acting throughout the element of volume $\delta v$.

We shall take the magnetic permeability of the medium to be unity.

The field equations are

$$\left.\begin{aligned} \text{Curl } H &= \frac{1}{c}\frac{\partial D}{\partial t} \\ \text{Curl } E &= -\frac{1}{c}\frac{\partial H}{\partial t} \end{aligned}\right\} \quad (5)$$

where $c$ is the velocity of light in vacuo

Also
$$D = K(E+F) \quad (6)$$

$$\left.\begin{aligned} \text{div } H &= 0 \\ \text{and} \quad \text{div } D &= 0 \end{aligned}\right\} \quad (7)$$

Eliminating H from (5) and making use of (6), we get

$$\nabla^2 E - \frac{K}{c^2}\frac{\partial^2 E}{\partial t^2} = \frac{K}{c^2}\frac{\partial^2 F}{\partial t^2} + \text{grad div } E \quad (8)$$

To solve (8), following Lorentz,[1] we shall introduce a new vector A given by

$$\nabla^2 A - \frac{K}{c^2}\frac{\partial^2 A}{\partial t^2} = -F \quad (9)$$

In order that (8) and (9) may simultaneously be true,

$$E = \text{grad div } A - \frac{K}{c^2}\frac{\partial^2 A}{\partial t^2} \quad (10)$$

and

$$H = \frac{K}{c}\frac{\partial}{\partial t}[\text{curl } A] \quad (11)$$

Equation (9) is of a well-known form and its solution is

$$A = \frac{1}{4\pi}\int \frac{1}{r} F_{(t-\frac{r}{u})} dv \quad (12)$$

where the integration is taken over the whole space in which F differs from zero and where $u = \frac{c}{\sqrt{K}}$ is the velocity of electro-magnetic waves in the medium, $r$ is the distance from $dv$ of the point at which A is required and $F_{(t-\frac{r}{u})}$ is the value of F at time $t-\frac{r}{u}$

When F is a periodic electric intensity $F_o \cos pt$ in the direction of the z-axis, confined to a single volume element $\delta v$ at the origin of co-ordinates.

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[1] H. A. Lorentz—Les Theories Statistique en Thermodynamique, pp. 42–43.

$F_x=0, \quad F_y=0 \quad \text{and} \quad F_z=F_o \cos pt$

Hence from (12)

$$A_x=0, \qquad A_y=0, \qquad A_z=\frac{F_o\delta v}{4\pi r}\cos p\left(t-\frac{r}{u}\right)$$

From (10),

$$E_x=\frac{\partial^2 A_z}{\partial z\partial x},\ E_y=\frac{\partial^2 A_z}{\partial y\partial z}\ \text{and}\ E_z=\frac{\partial^2 A_z}{\partial z^2}-\frac{1}{u^2}\frac{\partial^2 A_z}{\partial t^2}$$

The magnetic intensities can, if necessary, be easily deduced from (11). For distances from the origin large in comparison with the wave-length, $\frac{1}{r^2}$ and $\frac{1}{r^3}$ can be neglected in comparison with $\frac{1}{r}$ and hence

$$E_x=-\frac{xz}{r^3}\omega,\ E_y=-\frac{yz}{r^3}\omega,\ \text{and}\ E_z=\left(\frac{1}{r}-\frac{z^2}{r^3}\right)\omega \tag{13}$$

where $\omega=\frac{p^2F_o\delta v}{4\pi u^2}\cos p\left(t-\frac{r}{u}\right)$

The intensity of the radiation would be proportional to $E_x^2+E_y^2+E_z^2$ which is given by

$$\frac{x^2+y^2}{r^4}\omega^2=\frac{\sin^2\theta}{r^2}\omega^2 \tag{14}$$

where $\theta$ is the angle between the direction of the ray and the axis of $z$ (the direction of the applied electric intensity).

In the case of scattering by a single volume element $\delta v$,

$F_o=-\frac{\delta K}{K_o}E$ and the ratio of $E_x^2+E_y^2+E_z^2$ to $E^2$ the square of the amplitude of the incident wave is given by

$$\frac{\sin^2\theta}{r^2}\left(\frac{2\pi}{\lambda_1}\right)^4\left(\frac{\delta K}{K_o}\right)^2\frac{\delta v^2}{16\pi^2} \tag{15}$$

where $2\pi/\lambda_1$ has been substituted for $p/u$. $\lambda_1$ is the wave-length of the incident vibration in the medium.

Let us now consider the scattering produced by the accidental deviations of density in an extended volume. Let us take the X-axis to be the direction of the primary beam. The density deviations would change both in magnitude as well as in position in a perfectly arbitrary manner and there would be no co-ordination of phase between the vibrations scattered by the various elements. As a consequence, over any finite time-interval, the energies and not the amptitudes of the scattered radiations from the different elements of volume would be

additive. If $\delta\rho$ denotes the deviation of density from its uniform value $\rho_0$ in a volume element $\delta v$ then we can easily show[1] by applying Boltzmann's principle of entropy-probability that the mean square of deviation of density is given by

$$\overline{(\delta\rho^2)} = \frac{RT\beta}{N\delta v}\rho_0^2 \qquad (16)$$

The relation between density and dielectric constant is given by Lorentz's equation

$$\frac{K_0 - 1}{(K_0 + 2)\,\rho_0} = \text{constant.}$$

$$\text{Hence } \frac{\partial K}{\partial \rho} = \frac{(K_0 - 1)\,(K_0 + 2)}{3\rho_0}$$

and

$$\delta K = \frac{\partial K}{\partial \rho}\delta\rho$$

$$\overline{\delta K^2} = \frac{(K_0 - 1)^2 (K_0 + 2)^2}{9\rho_0^2}\,\delta\rho^2$$

$$= \frac{(K_0 - 1)^2\,(K_0 + 2)^2}{9}\,\frac{RT\beta}{N\delta v}$$

Substituting in (15) $\overline{\delta K^2}$ for $\delta K^2$ we get for the ratio of the average intensity of the scattered radiation to that of the incident

$$\frac{\pi^2}{9}\,\frac{RT\beta}{NK^2\lambda_1^4}\,(K_0 - 1)^2\,(K_0 + 2)^2\,\frac{\sin^2\theta}{r^2}\,\delta v$$

and since the radiations from different volume elements are additive

$$\frac{\pi^2}{9}\,\frac{RT\beta}{N\lambda^4}\,(K_0 - 1)^2\,(K_0 + 2)^2\,\frac{\sin^2\theta}{r^2} \text{ per unit volume} \qquad (17)$$

where $\lambda$ is the wave-length of the incident vibration in vacuo. The radiation in the direction of the $z$ axis is zero and is a maximum in the $xy$ plane.

When the incident light is unpolarised, the ratio of the intensity of the light scattered in a transverse direction to the intensity of the incident beam is given by

$$\frac{\pi^2}{18}\,\frac{RT\beta}{N\lambda^4}\,(K_0 - 1)^2 (K_0 + 2)^2\,\frac{1}{r^2}$$

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[1] Einstein—Ann. der Physik, Vol. 1910, p. 1275; also C. V. Raman and K. R. Ramanathan—Phil. Mag., Jan. 1923.

In a direction making an angle $\chi$ with the incident beam, this becomes

$$\frac{\pi^2}{18}\frac{RT\beta}{N\lambda^4}(K_0-1)^2(K_0+2)^2\left\{\frac{1+\cos^2\chi}{r^2}\right\} \tag{18}$$

To get the extinction co-efficient, we have only to find the total scattering from a stratum of thickness $dx$ and unit area of cross-section. Integrating (18) over the surface of a sphere of radius $r$, the ratio of the energy scattered by such a stratum to the incident energy is given by

$$\frac{dI}{I_0}=\frac{8\pi^3}{27}\frac{RT\beta}{N\lambda^4}(K_0-1)^2(K_0+2)^2 d\chi$$

$$\therefore I=I_0e^{-hx}$$

$$\text{where } h=\frac{8\pi^3}{27}\frac{RT\beta}{N\lambda^4}(K_0-1)^2(K_0+2)^2$$

We might substitute $\mu^2$ for $K_0$ in the above expressions where $\mu$ is the refractive index of the medium for the particular frequency.

### 3. *Scattering by Isotropic Molecules.*

Considering the problem from a molecular standpoint, the effect of an incident electro-magnetic wave on the molecules of a medium is to produce a displacement of the electrons in the molecules which is equivalent to creating an oscillating electric doublet in each molecule with a period the same as that of the wave. When the molecules are isotropic, the axes of the doublets coincide in direction with that of electric intensity, but when they are anisotropic, the displacements of the electrons are not in general in that direction, but the effect may approximately be taken to be equivalent to creating three doublets with their axes along three principal directions in each molecule. The field to which any molecule is subject is the resultant of that due to the incident wave and that due to the polarisation of the neighbouring molecules. The latter is taken account of in Lorentz's well-known treatment of dispersion in homogeneous, isotropic media. In the case of a gas at atmospheric pressure, its effect is negligible. The treatments of the scattering of light by isotropic molecules by the late Lord Rayleigh, Natanson, Sir J. J. Thomson and others do not take into account the influence of the surrounding molecules. Einstein's treatment of the subject does consider the effect due to the polarisation of the surrounding dielectric, but the treatment is non-molecular, and the results apply only to the case of a medium composed of isotropic molecules. With a view to extension to the case when the molecules are anisotropic, a molecular treatment of the problem is given below, taking into account the effect of the neighbouring molecules.

Consider a plane polarised wave travelling in the direction $Ox$. Let Z be the electric intensity in the wave parallel to $Oz$ and proportional to $\cos pt$. Under the influence of the wave, each molecule

becomes equivalent to a doublet with its axis parallel to $Oz$. Let A be the moment induced in a molecule when it is placed in a field of unit intensity. If the medium be of uniform density and if $n_0$ denotes the number of molecules per unit volume and $M_0$ the electric moment of each doublet, the actual intensity at any point O in the medium is given by

$$Z + \frac{4\pi}{3} n_0 M_0$$

and

$$M_0 = A\left( Z + \frac{4\pi}{3} n_0 M_0 \right)$$

$$= AZ \Big/ \left(1 - \frac{4\pi}{3} n_0 A\right) \tag{19}$$

Now $K_0$ the square of the refractive index of the medium for waves of frequency $p/2\pi$ is given by

$$\frac{K_0 - 1}{K_0 + 2} = \frac{4\pi}{3} n_0 A \tag{20}$$

and hence

$$M_0 = AZ \frac{(K_0 + 2)}{3} \tag{21}$$

A vibrating electric doublet radiates out energy. According to Hertz's well-known solution, the electric intensity at time $t$ at a point $r$ distant (great in comparison with $\lambda$) from the doublet is

$$\frac{p^2 M_{0\,t-\frac{r}{c}} \sin\theta}{c^2 r} \tag{22}$$

where $c$ is the velocity of light in vacuo, $\theta$ is the angle between $Oz$ and the direction of the ray and $M_{0\,t-\frac{r}{c}}$ stands for the value of the moment at time $t - \frac{r}{c}$.

When the molecules of the medium are uniformly distributed and we consider the effect due to a volume whose dimensions are large compared with A, it vanishes in all directions except in the direction of primary propagation where the secondary waves from the different molecules in the wave-front combine with the original wave and give rise to a plane wave moving with an altered velocity. In any actual fluid medium, however, owing to the thermal movements of the molecules, and the consequent fluctuations of density at any point, there is a finite radiation of energy in all directions. If $n_0$ represents the average number of molecules per unit volume in a volume element $\delta v$ and $\overline{\delta n^2}$ the mean square of the deviations of that number, then as before

$$\frac{\overline{\delta n^2}}{n_0^2} = \frac{RT\beta}{N\delta v} \tag{23}$$

Consider a volume element $\delta v$ at O small in comparison with a wave-length cube, but large compared to the dimensions of a molecule. Let $n$ be the number of molecules per unit volume in $\delta v$ and let $n$ be equal to $n_0 + \delta n$. The electric intensity at P due to scattering by the molecules contained in $\delta v$ would be given by

$$\frac{p^2}{c^2 r} \sin\theta \, \delta v \, (\mathrm{M}n - \mathrm{M}_0 n_0) \tag{24}$$

where M is the electrical moment appropriate to the density $n$. When we are considering the average effect over finite intervals of time, the distinction between M and $^{\mathrm{M}}t - \frac{r}{c}$ may be dropped. Now

$$(24) \quad = \frac{p^2}{c^2 r} \sin\theta \left[ (\mathrm{M}_0 + \delta\mathrm{M})(n_0 + \delta n) - \mathrm{M}_0 n_0 \right] \delta v$$

$$= \frac{p^2}{c^2 r} \sin\theta \, (\mathrm{M}_0 \delta n + n_0 \delta\mathrm{M}) \delta v \tag{25}$$

Differentiating (19) and applying (20)

$$\delta\mathrm{M} = \frac{(\mathrm{K}_0 - 1)(\mathrm{K}_0 + 2)}{9} \mathrm{AZ} \frac{\delta n}{n_0}.$$

$$\therefore n_0 \delta\mathrm{M} + \mathrm{M}_0 \delta n = \left(\frac{\mathrm{K}_0 + 2}{3}\right)^2 \mathrm{AZ} \delta n$$

$$= \frac{(\mathrm{K}_0 - 1)(\mathrm{K}_0 + 2)}{12\pi} \mathrm{Z} \frac{\delta n}{n_0} \tag{26}$$

Let us consider the effect due to (25). If E is the electric intensity at P due to radiation from $\delta v$, the energy is proportional to $\mathrm{E}^2$. It is thus

$$\frac{p^4 \sin^2\theta}{c^4 r^2} (\mathrm{M}_0 \delta n + n_0 \delta\mathrm{M})^2 \delta v^2$$

$$= \frac{p^4 \sin^2\theta}{c^4 r^2} \frac{(\mathrm{K}_0 - 1)^2 (\mathrm{K}_0 + 2)^2}{144\pi^2} \mathrm{Z}^2 \frac{\delta n^2}{n_0^2} \delta v^2$$

Since $\delta n$ varies from instant to instant according to the laws of chance the average expectation of $\mathrm{E}^2$ over a sufficiently long interval of time is

$$\overline{\mathrm{E}^2} = \frac{{}^{\prime}\sin^2\theta}{c^4 r^2} \frac{(\mathrm{K}_0 - 1)^2 (\mathrm{K}_0 + 2)^2}{144\pi^2} \mathrm{Z}^2 \frac{\overline{\delta n^2}}{n_0^2} \delta v^2$$

By (23),

$$\overline{\mathrm{E}^2} = \frac{p^4 \sin^2\theta}{c^4 r^2} \frac{(\mathrm{K}_0 - 1)^2 (\mathrm{K}_0 + 2)^2}{144\pi^2} \mathrm{Z}^2 \frac{\mathrm{RT}\beta}{\mathrm{N}} \delta v$$

When we consider the effect due to a volume V whose dimensions are large in comparison with $\lambda$, the ratio of the square of the electric vector in the scattered radiation to that in the incident is

$$\frac{\overline{E^2}}{Z^2} = \frac{p^4 \sin^2\theta}{c^4 r_2} \frac{(K_0-1)^2 (K_0+2)^2}{144\pi^2} \frac{RT\beta}{N} V.$$

$$= \frac{\pi^2}{9} \frac{RT\beta}{N\lambda^4} (K_0-1)^2 (K_0+2)^2 \ V. \ \frac{\sin^2\theta}{r^2}$$

where $\lambda$ is the wave-length of the light in vacuo.

## 4. *Scattering by Anisotrophic Molecules.*

Let $O'\xi$, $O'\eta$, $O'\zeta$ denote the three principal directions in a molecule whose centre is $O'$.

Let A, B, C be the moments induced in the molecule when placed in a field of unit intensity parallel to $O'\xi$, $O'\eta$, $O'\zeta$ respectively.

As before, let $Oz$ be the direction of the incident polarised plane wave and Z the electric intensity along $Oz$. In a medium composed of isotropic molecules the axis of the induced doublet in each molecule would be parallel to Z ; there would be no component along $Oz$ or $Oy$. In a medium composed of anistropic molecules, however, there would in general be components both along the $x$ and the $y$ axes. But when the axes of the molecules are oriented *at random* the components of the induced moments along the $x$ and $y$ directions would be as much positive as negative and hence the polarisation fields parallel to the $x$ and $y$ axis which may be taken as $\frac{4}{3}\pi n_0 \overline{M_x}$ and $\frac{4}{3}\pi n_0 \overline{M_y}$ respectively would vanish. We would however still have $\frac{4}{3}\pi n_0 \overline{M_z}$ because $M_z$ can have only positive values. The effect of the polarisation of the surrounding molecules is then to produce an additional field of $\frac{4}{3}\pi n_0 \overline{M_z}$. The resultant electric field at a point in the medium is therefore

$$Z + \frac{4}{3}\pi n_0 \overline{M_z} \tag{27}$$

To calculate $M_z$, we note that if the molecules are oriented at random,

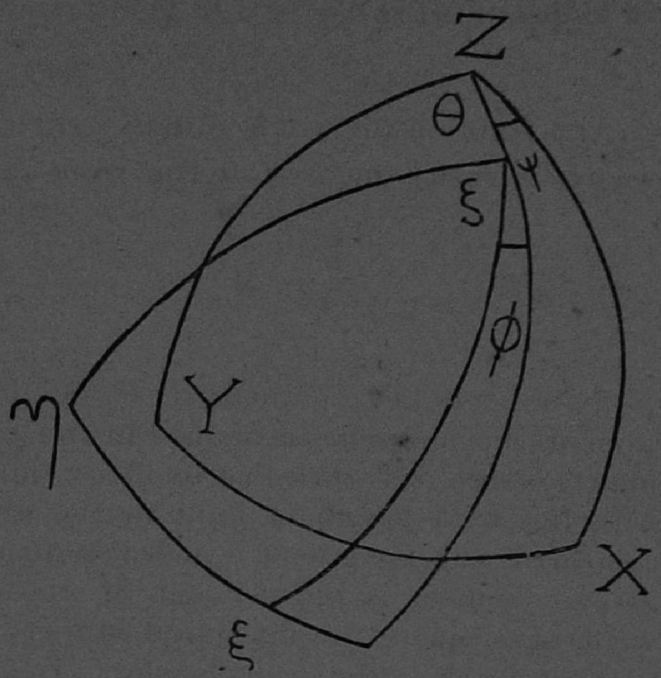
$$\overline{M_z} = \frac{A+B+C}{3}\left[Z + \frac{4}{3}\pi n_0 \overline{M_z}\right]$$

$$= \frac{A+B+C}{3} Z \quad \frac{K_0+2}{3}$$

and

$$\frac{K_0-1}{K_0+2} = \frac{4\pi n_0}{3}\left[\frac{A+B+C}{3}\right] \tag{28}$$

Consider a molecule, the direction of whose principal axes is defined by the Eulerian angles $\theta$, $\phi$, $\Psi$.[1]




In figure 1, $x$, $y$, $z$ represent the points where $O'x$, $O'y$, $O'z$ cut a sphere of unit radius, and $\xi$, $\eta$, $\zeta$ the points where the axes of the molecule cut the same sphere.

The moments induced in the molecule parallel to $O'\xi$, $O'\eta$, $O'\zeta$ are

$$-AZ\left(\frac{K_0+2}{3}\right)\sin\theta\cos\phi$$

$$BZ\left(\frac{K_0+2}{3}\right)\sin\theta\sin\phi \qquad (29)$$

$$CZ\left(\frac{K_0+2}{3}\right)\cos\theta$$

When these are resolved along $Ox$, $Oy$, $Oz$ the components are

$$M_x=Z\left(\frac{K_0+2}{3}\right)\Big[\sin\theta\cos\theta\cos\Psi\,(C-A\cos^2\phi-B\sin^2\phi)$$
$$+(A-B)\sin\theta\sin\Psi\sin\phi\cos\phi\Big]$$

$$M_y=Z\left(\frac{K_0+2}{3}\right)\Big[\sin\theta\cos\theta\sin\Psi\,(C-A\cos^2\phi-B\sin^2\phi)$$
$$+(A-B)\sin\theta\cos\Psi\sin\phi\cos\phi\Big]$$

$$M_z=Z\left(\frac{K_0+2}{3}\right)\Big[C\cos^2\theta+B\sin^2\theta\sin^2\phi+A\sin^2\theta\cos^2\phi\Big] \qquad (30)$$

which, for shortness, we may write

$$Z\left(\frac{K+2}{3}\right)L_1, \qquad Z\left(\frac{K_0+2}{3}\right)L_2, \qquad Z\left(\frac{K_0+2}{3}\right)L_3$$

[1] Lord Rayleigh and Sir J. J. Thomson. *loc. cit.*

The mean value of $M_x$ and $M_y$ taken over all orientations is zero, while that of $M_z$ is $Z\left(\frac{K_0+2}{3}\right)\left(\frac{A+B+C}{3}\right)$.

At a point on the $y$-axis distant $r$ from $O^1$, the $x$-component of the electric intensity due to scattering from a molecule at $O^1$ is

$$\frac{p^2}{c^2 r} M$$

In order to get the intensity at any instant of the light scattered from all the molecules contained in an element of volume $\delta v$ surrounding $O^1$, where $\delta v$ is such that its linear dimensions are small compared with the wave-length of light in the medium, but is yet so large compared with the size of a molecule that the fluctuations of density in one element is independent of those in neighbouring elements, we have to square the algebraical sum of the components of the electric vector from the different molecules. To get the average intensity over a finite interval of time, we have to calculate the average value of this quantity in a large number of independent trials in each of which the closeness of packing of the molecules and their orientations are re-distributed according to the principles of statistical mechanics. Thus, the $x$-component of the electric vector from all the molecules contained in $\delta v$ is

$$\frac{p^2}{c^2 r} \Sigma M_x$$

Since $\delta v$ contains a large number of molecules with their orientations at random, $\Sigma M_x$ would in general be small, since positive and negative values of $M_x$ are equally probable. But it is also possible that the values of $M_x$ are all positive, or all negative, or that the sum of all the positive values is just equal to the sum of all the negative values. These are extreme cases; at any trial, there would in general be a slight excess of the sum of all the positive values over the negative or *vice versa*. Thus, although in a large number of trials, $\Sigma M_x$ would be zero, $\Sigma M_x^2$ would not be. As the late Lord Rayleigh[1] has shown, when the value of $M_x$ is as *often* positive as negative,

$$\left(\Sigma M_x\right)^2 = n.\overline{M_x^2}\,\delta v$$

where $n\,\delta v$ is the number of molecules contained in $\delta v$.

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[1] Theory of Sound, Vol. I, p. 36.

Averaged over all orientations of molecules,

$$\overline{X/^2} = \frac{p^4}{c^4 r^2} Z \left(\frac{K+2}{3}\right)^2 f n_0 \, \delta v$$

where

$$f = \frac{1}{15} (A^2 + B^2 + C^2 - AB - BC - CA)$$

Form a finite volume V,

$$\overline{X/^2} = \frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0+2}{3}\right)^2 f n_0 V \qquad (31)$$

The Z-component of the electric vector at P in the wave scattered from a molecule at O' is, from (30),

$$\frac{p^2}{c^2 r} M_z = \frac{p^2}{c^2 r} Z \left(\frac{K+2}{3}\right) L_3$$

where K is the value of the optical dielectric constant appropriate to the density in $\delta v$. The value of $L_3$ averaged over all orientations is $(A+B+C)/3$ and the above expression can be written

$$\frac{p^2}{c^2 r} . Z \left(\frac{K+2}{3}\right) \left[ \frac{A+B+C}{3} + \left( L_3 - \frac{A+B+C}{3} \right) \right]$$

The square of the $z$-component of the electric vector from all the molecules contained in $\delta v$ is therefore

$$\frac{p^4}{c^4 r^2} . Z^2 \left(\frac{K+2}{3}\right)^2 \left[ \left( \frac{A+B+C}{3} \right)^2 n^2 \delta v^2 \right.$$

$$\left. + \left\{ \Sigma \left( L_3 - \frac{A+B+C}{3} \right) \right\}^2 + 2 \left\{ \Sigma \left( L_3 - \frac{A+B+C}{3} \right) \left( \frac{A+B+C}{3} \right) \right\} \right]$$

The third term is zero when averaged over all orientations. In the second term, $L_3 - \frac{A+B+C}{3}$ varies from molecule to molecule and may either be positive or negative, the average value over a large number of molecules with all possible orientations being zero. In such a case

$$\left[ \Sigma \left( L_3 - \frac{A+B+C}{3} \right) \right]^2 = n \, \delta v \left[ \overline{L_3^2} + \left( \frac{A+B+C}{3} \right)^2 \right.$$

$$\left. - 2\overline{L_3} \left( \frac{A+B+C}{3} \right) \right] = n \, \delta v . \frac{4}{3}$$

because

$$\overline{L_s^2} = \frac{1}{15}(3A^2 + 3B^2 + 3C^2 + 2AB + 2BC + 2CA)$$

and

$$\overline{L_s} = (A + B + C)/3.$$

The first term varies from one volume element to another owing to the fluctuations of density and the attendant fluctuations of dielectric constant, and as in the case of isotropic molecules (Sec. 3) the expectation of the square of the $z$-component in the light scattered from $\delta v$ arising out of this cause is

$$\frac{p^4}{c^4 r^2} Z^2 \left(\frac{K_0 + 2}{3}\right)^4 \left(\frac{A + B + C}{3}\right)^2 . \frac{RT\beta}{N} n_0^2 \delta v$$

The total value of $\overline{Z/^2}$ from a volume V is therefore

$$\overline{Z/^2} = \frac{p^4}{c^4 r^2} Z \left(\frac{K_0 + 2}{3}\right)^2 n_0 V \left[\left(\frac{A + B + C}{3}\right)^2 \gamma + \frac{4}{3} f\right] \quad \ldots \quad (32)$$

where

$$\gamma = \frac{RT\beta}{N} n_0 \left(\frac{K_0 + 2}{3}\right)^2.$$

The ratio of the weak component to the strong in the light scattered along O$y$ is

$$\frac{\overline{X^{1\,2}}}{\overline{Z^{1\,2}}} = \frac{f}{\gamma\left(\frac{A + B + C}{3}\right)^2 + \frac{4}{3} f.}$$

When the incident light is unpolarised, the ratio is

$$r = \frac{2f}{\gamma\left(\frac{A + B + C}{3}\right)^3 + \frac{7}{3} f.} \quad \ldots \quad (33)$$

When the substance is in the form of a vapour so rare as to obey Boyle's law, this becomes

$$\frac{2f}{\left(\frac{A + B + C}{3}\right)^2 + \frac{7}{3} f}$$

Denoting this by $r_1$, $r$ becomes

$$r=\frac{6r_1}{\gamma(6-7r_1)+7r_1} \quad \text{or} \quad \frac{\gamma r}{6-7r}=\frac{r_1}{6-7r_1} \qquad \ldots \quad (34)$$

The intensity of the transversely scattered light from a volume V at a distance $r$ large compared with the linear dimensions of V is

$$\frac{p^4}{c^4 r^2} Z^2\left(\frac{K_0+2}{3}\right)^2_{n_0} V. \left\{\left(\frac{A+B+C}{3}\right)^2 \gamma+\frac{13}{3}f\right\}$$

$$=\frac{Z^2}{r^2}\left\{\frac{\pi^2 RT\beta}{9\,N\lambda^4}(K_0-1)^2(K_0+2)^2+\frac{\pi^2}{n_0\lambda^4}(K_0-1)^2\,\frac{13r_1}{6-7r_1}\right\}V.$$

Substituting $r_1$ by $r$ and introducing $I_0$ the intensity of the incident unpolarised light, this becomes

$$\frac{I_0\,V}{r^2}\left\{\frac{\pi^2 RT\beta}{18N\lambda^4}(K_0-1)^2\,(K_0+2)^2\left(\frac{6+6r}{6-7r}\right)\right\} \qquad \ldots \quad (35)$$

—— the same expression as was first proposed by Prof. Raman[1] from general considerations to represent the scattering of light in liquids.

In a direction making an angle $\chi$ with the incident light, the intensity is easily seen to be

$$\frac{I_0 V}{r^2}\left[\frac{\pi^2 RT\beta}{18N\lambda^4}(K_0-1)^2(K_0+2)^2\left\{\frac{6-6r}{6-7r}(1+\cos^2\chi)+\frac{12r}{6-7r}\right\}\right] \ldots \quad (36)$$

and the coefficient of extinction becomes

$$\frac{8\pi^3}{27}\cdot\frac{RT\beta}{N\lambda^4}(K_0-1)^2\,(K_0+2)^2\left\{\frac{6+3r}{6-7r}\right\}.$$

### 5. *Comparison with Experiment.*

Prof. Raman and Mr. Seshagiri Rao[2] have compared the experimental values of the intensity of light transversely scattered by a number of liquids at the ordinary temperature with the values calculated according to (5), and shown that there is satisfactory agreement between the two except in the case of carbon disulphide which shows a very large depolarisation. In table I are included these values and also the values

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[1] "Molecular Diffraction of Light," p. 58, and C. V. Raman and K. Seshagiri Rao, Phil Mag., March 1923.

[2] Phil. Mag., March 1923.

obtained by Messrs. Martin[1] and Lehrman. To reduce the two sets of values to the same standard, the intensities of scattering for ether have been assumed to be the same.

*Table I.--Intensity of transversely scattered light in liquids.*

The intensities are expressed in terms of that of the polarised scattering of air at N.T.P.

| Liquid. | Temp. °C. | $r = \frac{\text{Weak Component}}{\text{Strong Component}}$ (per cent.) | | | Intensity (calculated). | Intensity (observed.) | Author. |
|---|---|---|---|---|---|---|---|
| | | R & R | M & L | Adopted. | | | |
| Water ... ... | 30° | 12·5 | | 11·0 | 159 | 165 | R & R[2] |
| | | | 6·7 | | | 165 | M & L[3] |
| Ether ... ... | 30° | 8·3 | | 9·0 | 930 | 860 | R & R |
| | | | 10·0 | | | 860 | M & L (assumed) |
| Methyl Alcohol | 30° | 15·1 | | 11·0 | 512 | 495 | R & R |
| | | | 7·1 | | | 462 | M & L |
| Ethyl Alcohol. | 30° | 13·0 | | 10·0 | 608 | 620 | R & R |
| | | | 7·8 | | | 485 | M & L |
| *n*—Propyl alcohol. | 18° | ... | 8·5 | 8·5 | 546 | 630 | M & L |
| Iso-butyl Alcohol. | 18° | ... | 3·5 | 8·5 | 610 | 679 | M & L |
| Iso-amyl Alcohol. | ... | ... | 9·0 | 9·0 | 595 | 722 | M & L |
| *n*—Hexane ... | ... | ... | 10 | 10 | 835 | 969 | M & L |
| Cyclo-hexane ... | ... | ... | 8 | 8 | 816 | 750 | M & L |
| Benzene ... | 30° | 39·8 | | 48·0 | 3,600 | 3,135 | R & R |
| | | | 48·5 | | | 2,477 | M & L |
| Toluene ... | 30° | 40·0 | | 49·0 | 4,170 | 2,970 | R & R |
| | | | 49·0 | | | 2,804 | M & L |
| Chloro-benzene. | ... | ... | 54 | ... | ... | 3,535 | M & L |
| $CS_2$ ... ... | 30° | 70 | | 71·0 | 23,000 | 16,000 | R & R |
| | | | 71·0 | | | 10,850 | M & L |

[1] Journ. Phys. Chemistry, Vol. 26, pp. 75–88 (1922).
[2] R & R.; C. V. Raman and K. S. Rao.
[3] M. & L.; W. H. Martin and S. Lehrman.

The last four liquids which have a large depolarisation show a scattering power lower than that calculated.

In table II, the polarisation of the transversely scattered light in a number of liquids is calculated from the corresponding values in their vapours according to (4) and the results compared with experiment.

*Table II.*

| Substance. | $\frac{\text{Weak Component}}{\text{Strong Component}}$ (per cent). | | |
|---|---|---|---|
| | Vapour. | Liquid at 30°C (calculated). | Liquid at 30°C (observed). |
| Ether ... ... ... ... ... | 3·0 | 26·7 | 9·0 |
| Benzene ... ... ... ... ... | 6·5 | 50·4 | 48 |
| $CS_2$ ... ... ... ... ... | 12·0 | 52 | 72 |
| $CHCl_3$ ... ... ... ... ... | 3·0 | 26 | 15 |
| $CCl_4$ ... ... ... ... ... | 3·1 | 37 | 11 |

Except in the case of benzene, the calculated values show no agreement with the observed ones. With carbon disulphide, the observed value is higher than the calculated, while with the others, it is lower. This disagreement between observation and theory seems to show that the molecules in a liquid are not oriented at random. We should, however, still have expected the observed intensities to agree with the calculated, provided we make use of the *observed* values of the imperfection of polarisation. Although there is a good agreement for liquids showing a moderate depolarisation, it is no longer so for liquids showing strong depolarisation. It is remarkable that for these liquids, the observed intensities are *smaller* than the calculated ones.

## 6. *Synopsis.*

1. An electromagnetic theory of the scattering of light in fluids has been worked out without assuming a molecular structure on the basis of Lorentz's treatment of the scattering of light in gases and the Einstein-Smoluchowski formula for scattering derived.

2. The same result is shown to follow if the fluid medium be supposed to be composed of isotropic molecules.

3. The treatment is extended to the case when the molecules are anisotropic in which case it is shown that if the orientations of the molecules are entirely at random, the transversely scattered light is

imperfectly polarised, the ratio of the weak component to the strong being given by

$$r = \frac{2f}{r\left(\frac{A+B+C}{3}\right)^2 + \frac{1}{3}f}$$

The intensity of the scattered light in a direction making an angle $\chi$ with the incident beam is

$$\frac{I_0 V}{r^2}\left[\frac{\pi^2 RT\beta}{18N\lambda^4}(K_0-1)^2(K_0+2)^2\left\{\frac{6-6r}{6+7r}(1+\cos^2\chi)+\frac{12r}{6-7r}\right\}\right]$$

The expression reduces to the usual appropriate forms when the medium consists of isotropic molecules and when the medium is a vapour obeying Boyle's law.

The co-efficient of extinction is shown to be

$$\frac{8\pi^3}{27}\frac{RT\beta}{N\lambda^4}(K_0-1)^2(K_0+2)^2\left\{\frac{6+3r}{6-7r}\right\}$$

4. The theoretical results are compared with experiment. While there is good agreement between the observed and calculated values of the intensity of scattering for liquids having molecules of moderate anisotropy, there is a marked disagreement in the case of liquids with strongly anisotropic molecules.

The values of the imperfection of polarisation of liquids calculated from the corresponding vapour values show considerable deviation from the experimental values except in the case of benzene. This disagreement seems to show that the molecules in a liquid are not oriented at random.

I wish to express my best thanks to Prof. C. V. Raman for his kind interest in the work and for his valuable suggestions.

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# THE MOLECULAR SCATTERING OF LIGHT IN VAPOURS AND IN LIQUIDS AND ITS RELATION TO THE OPALESCENCE OBSERVED IN THE CRITICAL STATE

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## 1. *Introduction.*

It has long been known that in the immediate vicinity of the critical state, many substances exhibit a strong and characteristic opalescence. In recent years, the phenomenon has been studied by Travers and Usher* in the case of carefully purified $CS_2$, $SO_2$, and ether, by S. Young † and by F. B. Young ‡ in the case of ether, and in a quantitative manner by Kammerlingh Onnes and Keesom § in the case of ethylene. An explanation of the phenomenon on thermodynamic principles as due to the accidental deviations of density arising in the substance was put forward by Smoluchowski.‖ He obtained an expression for the mean fluctuation of density in terms of the compressibility of the substance, and later, Einstein ¶ applied Maxwell's equations of the electro-magnetic field to obtain an expression for the intensity of the light scattered in consequence of such deviations of density. He showed that the fraction $\alpha$ of the incident energy scattered in the substance per unit volume is

$$\frac{8\pi^3}{27} RT\beta \frac{(\mu^2-1)^2 (\mu^2+2)^2}{N\lambda^4} \qquad (1)$$

In this, R and N are the gas constant and Avogadro's number per gram-molecule, $\beta$ is the isothermal compressibility of the substance, $\mu$ is the refractive index and $\lambda$ is the wave-length of the incident light. Keesom ** tested this formula over a range of 2·35° above the critical point of ethylene and found good agreement except very close to the critical point.

* "Roy. Soc. Proc.," A, vol. 78, p. 247 (1908).
† *Ibid.*, p. 262.
‡ "Phil. Mag.," vol. 20, p. 793 (1910).
§ "Roy. Soc. Proc., Amsterdam," 1908.
‖ "Ann. der Physik," vol. 25, p. 205 (1908).
¶ "Ann. der Physik," vol. 33, p. 1275 (1910).
** "Ann. der Physik," vol. 35, p. 591 (1911).

Of an altogether different order of intensities is the phenomenon of light scattering in gases and vapours under ordinary pressures observed experimentally by Cabannes * and the present Lord Rayleigh.† The effect studied by these investigators is, in comparison with the phenomenon of critical opalescence, feeble, and requires powerful illumination and special arrangements to enable it to be observed in the laboratory. The measurements made by them show that the magnitude of the effect‡ is in substantial agreement with the theory of molecular scattering of light developed by the late Lord Rayleigh, according to which the extinction-coefficient $\alpha$ is given by

$$\frac{32\pi^3}{3} \frac{(\mu-1)^2}{n\lambda^4} \qquad (2)$$

where $n$ is the number of molecules per unit volume. The scattering of light in passage through *dust-free liquids* has also been observed by the present Lord Rayleigh § and W. H. Martin,‖ and it was found by the former that the intensity of scattering in the liquid studied (ether) was considerably smaller than that given by the formula (2), though, owing to the greater density of the liquid, the absolute magnitude of the effect is many times larger than in the vapour.

It is important to notice that these three phenomena, namely, critical opalescence, scattering of light by gases and vapours, and scattering by liquids, which are of such different orders of magnitude, and apparently so distinct, stand in reality in the closest relationship to each other. It has been pointed out by Prof. C. V. Raman¶ that the observed scattering power of liquids under ordinary conditions agrees with that calculated from the Einstein-Smoluchowski formula ; and further, that this law which reduces to Rayleigh's formula in the special case of a gas obeying Boyle's law, is much more generally applicable than the latter and should be regarded as the fundamental relation determining the magnitude of light scattering in all fluid media. It thus becomes a matter of great importance to make a thorough test of the Einstein-Smoluchowski formula over the widest possible range of experimental conditions. A series of investigations with this object has been undertaken at Calcutta.

The present paper describes the results of a study made of the scattering of light in ether, both in the liquid and in the saturated vapour phases at different temperatures from 30° up to the critical

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* "Comptes Rendus," vol. 160, p. 62 (1915) ; and "Ann. de Physique," vol. 15 (1920).

† "Roy. Soc. Proc.," A, vol. 94, p. 453 (1918).

‡ "Roy. Soc. Proc.," A, vol. 95, p. 155 (1918).

§ "Roy. Soc. Proc.," A, vol. 95, p. 95 (1918).

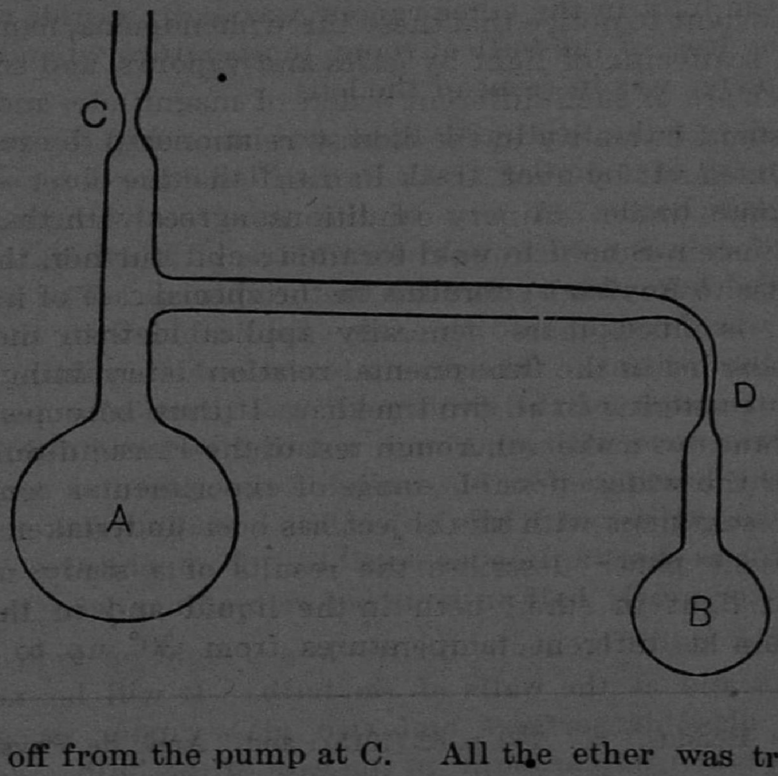
‖ "Journal of Physical Chemistry," 1919.

¶ "Nature," November 10, 1921, and "Roy. Soc. Proc.," A, April, 1922. See also "Molecular Diffraction of Light," by C. V. Raman, published by the Calcutta University Press, 1922, pp. 12 and 60.

point 193·6°, and also in the gaseous phase above the critical temperature up to 217° C. Ether was chosen as the first substance to be investigated, because it possesses a high refractivity and hence a large scattering power, is easily obtained pure, and can withstand the action of heat and moderately intense light without appreciable change. Moreover, the classical work of Ramsay and Young* on the pressure-volume relations of the substance over a wide range of temperature provides the necessary data for calculation.

## 2. *Experimental Arrangements.*

The ether used was Merck's pure ether, redistilled four or five times *in vacuo.* It was contained in a thick, uniform glass bulb of about 3 cm. external diameter. The necessary quantity of ether was introduced into it in the following manner. A glass apparatus of the form shown in the figure was made. The bulbs and connecting tube were well heated over a Bunsen flame and the air exhausted by means of a pump. Nearly four times the required quantity of ether was introduced into the bulbs, and in order to remove the dissolved air, the apparatus was exhausted until more than half the ether had evaporated and it was




then sealed off from the pump at C. All the ether was transferred to the bulb A, and a portion was distilled over into B by placing A in a vessel of warm water at 45—50° C. and B in a vessel of water at the room-temperature (about 30° C.). When B was nearly half filled, its inside was washed out with the distilled ether, which was then

* "Phil. Trans.", A., vol. 178, p. 57 (1887).

transferred back to A without allowing the undistilled ether to come into B. This process was repeated four or five times in order to get the ether perfectly dust-free, and finally, when the required quantity had collected in B, the bulb was sealed off at D.

The outside of the bulb was painted dead black, leaving three windows, two at the sides to let in and let out light, and one at the base for the observation of the scattered light. It was then mounted in the centre of a thick iron cross-tube, blackened inside, similar to the one employed by Lord Rayleigh (*loc. cit.*). The cross-tube was nearly 1·5 inches external diameter, and each arm of the cross was 7 inches long. Its ends were closed with glass windows, and it could be heated to any temperature up to 250° C. by passing an electric current through a coil of Eureka wire wound uniformly over it. The temperature could be maintained steady within less than half a degree for hours. The distribution of temperature was very uniform in the middle of the tube. The tube was mounted horizontally and sunlight was concentrated at the centre of the bulb by means of a lens. Different apertures could be introduced in front of the lens to regulate the quantity of light. Suitable diaphragms were also introduced inside the cross-tube to prevent diffuse light from reaching the eye. With this arrangement the track of the light in the ether vapour was easily visible through the window at the base of the bulb at room temperature when an aperture of 1 inch diameter was in front of the lens.

The intensity of the scattered light was measured by comparing it with the intensity of a similar track in distilled ether kept outside in a rectangular glass bottle. A lens of the same focal length as the one mentioned before was used to produce the track, and suitable apertures were introduced here also to regulate the brightness. The image of the second track was brought into the same field of view by means of two totally reflecting prisms. The prisms exercised very little absorption and the colour-match of the two tracks was practically perfect. The photometry was done with an Abney rotating sectored disc. In order to minimise the heating effect of sunlight, the apertures were made of the smallest size consistent with the visibility of the track, and the light was kept on for as short a time as possible. Temperatures were maintained steady for nearly half an hour before readings were taken.

A correction has to be made for the loss of light on reflection at the glass windows and at the walls of the bulb. It will be noticed that there are six glass-air surfaces and two glass-vapour or glass-liquid surfaces to be taken into account in the case of the bulb, and six glass-air surfaces and two glass-liquid surfaces in the case of the ether bottle used as standard. There would thus be an approximate compensation. To test if it is so, and to allow for any absorption which the right-angled prisms might exercise, a comparison was made of the light scattered by the ether in the bulb at room temperature and that scattered by the standard. The two were found to be equal within 2 per cent.

## 3. *Results.*

The observed data for the intensity of the scattering by the saturated vapour in terms of liquid ether as a standard are shown in Table I. The theoretical results indicated by the Einstein-Smoluchowski formula are shown in the third column after applying the correction for imperfect polarisation of the scattered light, as explained below in Art. 5. In order to calculate the theoretical value, it is necessary to know the compressibility, $\beta$ or $-(1/v\ dv/dp)_t$, and the refractive index, $\mu$, of the saturated vapour at the respective temperatures of observation, and similar data for the liquid used as a standard at 35° C. The compressibilities, $-(1/v\ dv/dp)$ of the vapour at different temperatures were determined by plotting Ramsay and Young's pressure-volume data on graph-paper and drawing tangents at the points of saturation. The values of $\mu$ were obtained by the application of Lorentz's refraction formula $(\mu^2-1)/\ \mu^2+2) = k\rho$, where $k$ has the value 1/3·317 for ether.

It will be seen that throughout there is a good agreement of the observed and calculated results. In column 4 of Table I, the ratio of the scattering power of the vapour saturated at $t°$ to the scattering power of the vapour saturated at 35°, and in column 5 the ratio of the vapour densities under the same conditions, taken from Ramsay and Young's data, are shown. If Rayleigh's law of scattering had been valid throughout this range, the figures in columns 4 and 5 should have

Table I.—Scattering by Saturated Ether Vapour.

| Temperature ($t°$ C.) | Scattering at $t°$ C. / Scattering by liquid ether at 35° C. | | Ratio of scattering at $t°$ C. to scattering at 35° C. | Ratio of density of vapour at $t°$ C. to density at 35° C. |
|---|---|---|---|---|
| | Observed. | Calculated from Einstein-Smoluchowski formula. | | |
| 33 | 0·038 | 0·036 | 1·00 | 0·92 |
| 54 | 0.075 | 0·074 | 1·97 | 1·81 |
| 75 | 0·150 | 0·140 | 3·95 | 3·22 |
| 91 | 0·22 | 0·23 | 5·79 | 4·79 |
| 108 | 0·45 | 0·45 | 11·8 | 7·1 |
| 123·5 | 0·71 | 0·71 | 18·7 | 10·0 |
| 144·5 | 1·31 | 1·29 | 34·5 | 15·7 |
| 164 | 2·7 | 3·0 | 71·0 | 24·0 |
| 170·5 | 3·9 | 4·0 | 103 | 28·0 |
| 179·2 | 9·1 | 7·9 | 239 | 35·3 |
| 183·5 | 13·0 | 12·2 | 342 | 39·8 |
| 186·5 | 21 | 19 | 553 | 44·2 |
| 190 | 42 | 39 | 1105 | 51·9 |
| 191 | 63 | 55 | 1658 | 53·3 |

agreed. Actually there is an enormous difference, showing that, at least in the case of ether, Rayleigh's law breaks down completely, and that the "principle of random phase," on which he founded his theory

of molecular scattering, is inapplicable except at very low pressures, where the deviation from Boyle's law is negligible. The scattering power of the vapour is greater, and at the higher temperatures enormously greater, than if the molecules of the gas scattered secondary waves in arbitrary phase-relationships with each other.

The experimental results of the scattering power of ether in the gaseous phase above the critical point are shown in the second column of Table II. In this case, in order to calculate the compressibilities and refractive indices, it is necessary to know the actual mass of ether used, and the volume of the bulb in which it is contained, and these were separately determined at the completion of the experiment, and were found to be 3·164 grm. and 13·98 c.c. respectively. The theoretical value of the scattering power as given by the Einstein-Smoluchowski formula is shown in column 3.

Table II.—Scattering by Ether above Critical Temperature.

| Temperature ($t$° C.). | Scattering at $t$° C / Scattering by liquid ether at 35°C | | Ratio of scattering at $t$° C. to scattering at 35° C. | Ratio of density of vapour at $t$° C. to density at 35° C. |
|---|---|---|---|---|
| | Observed. | Calculated from Einstein-Smoluchowski formula. | | |
| 194 | 378 | 290 at 195° | 9950 | 71·6 |
| 196 | 172 | 200 at 197° | 4530 | 71·6 |
| 198 | 126 | | | |
| 200 | 84 | 87 | 3316 | 71·6 |
| 202 | 64 | 65 | 1680 | 71·6 |
| 212·5 | 27 | 30 | 710 | 71·6 |
| 217 | 21 | 26 | 553 | 71·6 |

Considering the unavoidable experimental uncertainties such as a slight fluctuation of temperature, which has an enormous influence in the neighbourhood of the critical point, the presence of a trace of dissolved air or other impurity in the ether, and the difficulty of determining the value of the compressibility accurately, the agreement should be considered good. The figures in columns 4 and 5 further illustrate the fact that the scattering power of the gas throughout the range of temperature is far greater than would be the case if the "principle of random phase" were valid.

Finally, Table III shows the observed sctattering power of liquid ether.

Table III.—Scattering by Liquid Ether.

| Temperature ($t^\circ$ C.). | Scattering at $t^\circ$ C. / Scattering at 35° C. Observed. | Scattering at $t^\circ$ C. / Scattering at 35° C. Calculated from Einstein-Smoluchowski formula. |
|---|---|---|
| 33 | 1·00 | 1·00 |
| 61 | 1·23 | 1·34 |
| 80 | 1·85 | 1·65 |
| 91 | 1·90 | 1·83 |
| 104 | 2·3 | 2·13 at 100° |
| 125 | 3·0 | |
| 139 | 3·8 | |
| 145 | 4·9 | 8·2 at 150° |
| 153 | 6·3 | |
| 170 | 12·0 | 14·1 at 175° |
| 179 | 22 | |
| 185 | 38 | 27·2 |
| 190·5 | 82 | 73 at 190° |

The density data for liquid ether have been taken from Ramsay and Young's paper; the compressibilities below 100° from Amagat's determinations, and those above 100° from Ramsay and Young's work. There seems to be an inaccuracy in Ramsay and Young's compressibility data for liquid ether at 150°; the values of the pressure and volume do not plot into a smooth curve, and in the curve accompanying Ramsay and Young's paper one can notice an unusually rapid change of curvature in the close proximity of the vapourisation point. Making allowance for this, a satisfactory agreement appears between the theoretical and observed values of the scattering power.

Taking the results contained in the three tables together, it will be seen that the scattering rises rapidly as the critical point is approached, and the values for the saturated vapour, liquid and gaseous phases approach each other and converge to a very large value at this point. The intensity of the scattering under critical conditions is enormous being about 750 times that of liquid ether at ordinary temperature.

## 4. *Critical Opalescence.*

The Einstein-Smoluchowski formula (1), as it stands, gives an infinite value for the scattering power at the critical point. This is physically impossible, and both Smoluchowski and Einstein have pointed out that, in the immediate neighbourhood of the critical point, terms involving $(d^3p/dv^3)_t$ and higher order terms should be taken into account. It is, however, doubtful if even the inclusion of these terms would be sufficient, for the scattered light is markedly less blue in this region, which Einstein's theory does not contemplate. Ornstein and Zernike* have pointed out that the independence of density-fluctuations

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* "Roy. Soc. Proc., Amsterdam," vol. 17 (1914) and "Phys. Zeitschrift," vol. 18 (1917).

in different elements of volume assumed by Einstein is inadmissible in this region, and, taking these mutual influences into account, they have deduced a modified equation for the opalescence in which the term $-(dp/dv)_t$ is replaced by

$$-\left(\frac{dp}{dv}\right)_t + \frac{4\pi RT}{v^2}\,\frac{\epsilon^2}{\mu^2\lambda^2} \tag{3}$$

where $v$ is the molecular volume and $\epsilon$ is a measure of the radius of action of a molecule, beyond which its influence is negligible. Using this, the total fraction of light scattered per unit-volume, instead of being infinity at the critical point, has a finite value

$$\frac{2\pi}{27}\,\frac{\mu^2(\mu^2-1)^2\,(\mu^2+2)^2}{N\lambda^2\,\epsilon^2},\ v \tag{4}$$

Also the proportionality of the scattering light with $\lambda^{-4}$ gives place to one of proportionality with $\lambda^{-2}$

The change of colour of the opalescent light in the neighbourhood of the critical point is easily observable when the opalescent beam is reduced in intensity by means of the rotating disc photometer to equality with the scattered light from liquid ether. If we assume that the maximum value of the scattering coefficient is given by (4), we can easily obtain an estimate of $\epsilon$. Observations of the maximum intensity of the scattered light were made by heating the ether about 10° above the critical temperature, and then *very slowly* cooling it. With the particular quantity of ether used (3·164 grm. in 13·98 c.c.) the maximum scattering was found to be 750 times that of liquid ether at 35° C. Putting in the numerical values, and taking $\lambda$ equal to be 5000 Å.U., the scattering coefficient works out to be $8{\cdot}6 \times 10^{-3}$, and $\epsilon$ to be $4{\cdot}6 \times 10^{-7}$ cm.

However, this correction to the Einstein-Smoluchowski formula is of secondary importance, and does not affect the broad aspects of the question.

### 5. *Polarisation of the Scattered Light.*

It has been shown by Lord Rayleigh, that the light scattered by dust-free gases and vapours in a direction at right angles to the incident beam is, in most cases, imperfectly polarised. In the case of ether vapour, he found that the ratio of the weak component to the strong in the scattered light was 1·7 per cent. It was interesting to study how the imperfection of polarisation changes as the condition of the substance changes from liquid to vapour. At ordinary temperatures, the light scattered by liquid ether showed an imperfection of polarisation amounting to 8 per cent. As the temperature was raised, it remained constant until a temperature of about 125° was reached and then fell off, rapidly at first, and then more slowly to the value corresponding to that

of the vapour at the critical point. Table IV gives the results of the polarisation measurements on liquid ether at different temperatures.

Table IV.—Polarisation of Light Scattered by Liquid Ether.

| Temperature. | Weak component compared with strong. |
|---|---|
| 33° C. ... ... ... ... | 8 per cent. |
| 60 ... ... ... ... | 8 ,, |
| 80 ... ... ... ... | 7 ,, |
| 100 ... ... ... ... | 7·5 ,, |
| 120 ... ... ... ... | 7·5 ,, |
| 135 ... ... ... ... | 5 ,, |
| 145 ... ... ... ... | 3 ,, |
| 165 ... ... ... ... | 1·7 ,, |
| 189 ... ... ... ... | 1·3 ,, |

In the case of the vapour, measurements of polarisation were made from 160° to about 200° C. The values of the ratio of the weak component to the strong ranged from 1·3 to 1·0 per cent. There was no change in the value of the ratio on passing through the critical point.

The difference between the liquid and the vapour at the lower temperatures is striking. In the case of gases, the late Lord Rayleigh has shown that imperfection of polarisation can be explained on the assumption of asymmetry of the molecules. The increased value for the imperfect polarisation in liquids, and its rapid decrease with temperature, are results of great interest which await explanation.* Further studies on this point, with a number of other vapours and liquids, are being made by the writer.

This imperfection of polarisation has to be taken account of in calculating the intensity of the scattered light. In the case of gases, Cabannes has shown that the scattering is greater in the ratio $6(1+r)/(6-7r)$, where $r$ is the ratio of the weak component to the strong in the light scattered in a perpendicular direction. The question can be viewed in yet another way. The imperfectly polarised light can be looked upon as being caused by an admixture of a certain quantity of unpolarised light with the polarised light. If to a beam of polarised light of intensity A, there be added a beam of unpolarised light of intensity 2B, the resultant light will be imperfectly polarised and the ratio of the weak component to the strong would be given by $r = B/(A+B)$ and the intensity of the resultant light will be $A(1+2B/A) = A\left(1+\frac{2r}{1-r}\right)$. When $r$ is small this reduces to $A(1+2r)$. An expression of this form is found to agree with the intensity of the scattered light in gases and

* Since the above was written, a theory based on the conception of molecular æolotropy has been developed by Prof. C. V. Raman, which not only explains these phenomena, but predicts also that the imperfectness of polarisation, both in the case of liquids and vapours, should decrease and tend to a minimum at the critical point. Observations by the writer on benzene confirm this result.

liquids, when A is taken to be the scattering calculated from the Einstein-Smoluchowski formula. The factor $1+2r/(1-r)$ becomes of great importance when $r$ is large. It will be noticed that when $r$ is not very large, this expression becomes practically equal to the correction factor $6(1+r)/(6-7r)$ introduced by Cabannes. In the Tables I, II and III given above such a correction has been introduced. The imperfection of polarisation for ether vapour has been throughout taken to be 1·2 per cent and that of liquid has been taken as given in Table IV.

## 6. *Summary.*

1. Three instances of light scattering by homogeneous media are known ; opalescence of a substance near the critical point, scattering of light by gases, and scattering of light by liquids. The present investigation was undertaken to test the view put forward by Prof. C. V. Raman that these phenomena are fundamentally related to each other and that the intensity of scattering in all these cases should be represented by the Einstein-Smoluchowski formula, which is more general than the Rayleigh law of scattering and supersedes it except in the special case of gases obeying Boyle's law.

2. Experiments on the scattering of light by ether, in the vapour and liquid phases at different temperatures from 33° C. up to the critical temperature 193·6°, and in the gaseous phase from 193·6° to 217°, are described.

3. The results are in accord with the Einstein-Smoluchowski formula and not with the Rayleigh law of scattering.

4. The Einstein-Smoluchowski formula is inapplicable in the *immediate neighbourhood* of the critical point. The scattered light is markedly less blue here. Following the theoretical work of Ornstein and Zernike, from the maximum value of the intensity of the scattered light, the value of $\epsilon$ the radius of action of an ether molecule is deduced to be $4·6 \times 10^{-7}$ cm.

5. The light scattered at right angles to the incident beam is imperfectly polarised ; the ratio of the weak component to the strong is throughout nearly 1·2 per cent in the case of vapour, while, in the case of liquids, the ratio is 8 per cent at ordinary temperatures which remains constant till about 120°, and then falls off, rapidly at first and then slowly to about 1·2 per cent at the critical point. There is no change of imperfection of polarisation on passing through the critical point. The correction due to this in the expression for the intensity of the scattered light is given.

In conclusion, I have great pleasure in recording my indebtedness to Prof. C. V. Raman who suggested the research, and who continued to take an inspiring interest in its progress. The experimental work was carried out in the Physical Laboratory of the Indian Association for the Cultivation of Science, Calcutta.

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# THE MOLECULAR SCATTERING OF LIGHT IN BENZENE VAPOUR AND LIQUID.

BY K. R. RAMANATHAN.

ABSTRACT.

*Scattering of sunlight by benzene, vapour and liquid, from 35° to 283° C.*—The intensity of the light scattered at right angles was determined relative to that scattered by liquid ether at 35° C, by photometric comparison with the aid of reflecting prisms and a sectored disc. The relative intensity increased with the temperature at an accelerated rate; for the liquid, from 3·2 at 35° to 102 at 283° and, for the saturated vapour, from 0·95 at 182° to 11·9 at 267°. The scattered light is not completely polarized. The *imperfection of polarization* was measured by use of a double-image prism and a nicol. The ratio of the weaker to the stronger component, $r$, was found to decrease from 7·2 to 0·9 per cent for the vapour and from 43 to 2·8 per cent for the liquid as the temperature was raised from 35° to 280°. *Comparison with theories.* This imperfection has been attributed to the anisotropy of the molecules by Rayleigh, Born and others. The theory as extended by Raman to the general case of fluids leads to the relation $Sr/\rho\,(1+r) = \text{const.}$, where $S$ is the intensity and $\rho$ the density. This is found to agree satisfactorily with the observations for both vapour and liquid. Since for the vapour, the intensity $S$ increases with the temperature much more rapidly than the density, the Rayleigh law is not valid. The Einstein-Smoluchowski formula shows much better agreement, although, when calculated values of the refractive index and compressibility are inserted, it gives for the scattering in the vapour values which are 20 per cent or more too high.

*Formula for isothermal compressibility of a saturated vapour* is derived from Dietrici's equation of state. It is found to give the observed values for ether, isopentane and $CO_2$ in the temperature range 0·8 to 0·96 $T_c$ if an arbitrary numerical factor 1·25 is used. Introducing this forgives, this range, $(dp/d\rho)_t = 2{\cdot}5p\,(\rho_c - \rho)^2/(2\rho_c^{\,2}\rho - \rho^2\rho_c)$.

## 1. *Introduction.*

In his recent experiments on the molecular scattering of light in gases and vapours[1], Lord Rayleigh noticed the interesting fact that the light scattered in a direction perpendicular to the incident beam was not perfectly polarized. A similar effect has been observed, but in a

[1] Proc. Roy. Soc. A., vol. 94, p. 453, 1918.

much more marked degree by W. H. Martin[1] in the light scattered by dust-free liquids. When we compare a liquid like ether and its vapour at the ordinary temperature in this respect, we find a large difference. Ether vapour at the ordinary temperature shows an imperfection of 1·7 per cent, while liquid ether shows 8 per cent. The imperfection of polarization in gases has been explained,[2, 3] on the assumption of anisotropy of the molecules; the imperfection in liquids is no doubt to be attributed to the same cause. The general theory of light scattering in liquids has been discussed by Professor C. V. Raman,[4] who has also put forward an explanation[5] of the increased imperfection of polarization of the scattered light in this case and suggested a quantitative connection between the intensity of the transversely scattered light, its state of polarization and the density of the fluid. A brief account of this theory is given in the course of the paper. The experiments described here were undertaken with a view to securing data regarding the intensity and polarization of the transversely scattered light both in the liquid phase and saturated vapour phase of a suitable substance over a large range of temperatures. Benzene was chosen owing to the large value of its imperfection of polarization at ordinary temperatures. The result of the experiments has been to confirm the general validity of the explanation suggested.

## 2. *Experimental arrangements.*

The apparatus used in the work is the same as that used by the author in an investigation on the intensity of the light scattered in ether.[6] The benzene was sealed in a stout-walled uniform glass bulb of about 1·2 inches internal diameter and the bulb was mounted in the centre of an iron cross-tube (diameter 1·5 inches and each arm of the cross 15 inches long). The ends of the tube were closed with glass windows and it could be heated electrically by passing a current through a coil of nichrome wire, wound uniformly over it. Temperatures could be maintained steady for long intervals of time to within half a degree. The benzene used was Merck's pure grade and was distilled five or six times in vacuo in the manner described by Martin.[7]

The intensity of the scattered light was determined by comparing the luminosity of a track of sunlight passing through it with a similar track in liquid ether kept in a rectangular glass bottle at the room temperature. The sunlight was focussed by two exactly similar lenses

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[1] Journal of Physical Chemistry, vol. 24, 1920, p. 478 and Jan. 22.
[2] Lord Rayleigh : Phil. Mag., vol. 35, p. 373, 1919.
[3] Born : Deutsch. Phys. Gessell, vol. 19, p. 243, 1917 and vol. 20, p. 16, 1918.
[4] "Molecular Diffraction of Light," Calcutta University Press.
[5] "Nature," July 1922, p. 11.
[6] Proc. Roy. Soc., vol. 102, p. 151, 1922.
[7] Loc.cit.

of the same focal length and provided with adjustable apertures at the centre of the benzene bulb and at the centre of the ether bottle. By means of two totally-reflecting prisms, the two tracks were brought side by side and their luminosities compared visually by means of a rotating sectored disc photometer.

The polarization of the light scattered at right angles to the incident beam was measured by means of a double-image prism and nicol. The double-image prism was mounted at the same height as the benzene bulb with its axis horizontal and pointing towards the bulb. It was first adjusted so that the two images of the track were in a horizontal line and side by side with each other. The nicol was now inserted behind the double-image prism and so oriented that the vertical component was extinguished. On either side of this position, there is a position when the two images would be equal in intensity. If we denote the angle between these two equality-positions by $2\theta$ the ratio of the intensity of the horizontal component to that of the vertical is given by $\tan^2\theta$.

## 3. *Results.*

The results regarding the scattering in the saturated vapour of benzene and in liquid benzene are collected in the following two tables.

TABLE I.—SCATTERING IN SATURATED BENZENE VAPOUR.

$S_t$ = Scattering at t°c.
$S_0$ = Scattering in liquid ether at 35°C
$\rho_t$ = Density at t°c.
r = Ratio of weak component to strong in the transversely scattered light.

| Temperature t°c. | Observed $S_t/S_0$ | $S_t/S_{182}$. | $\frac{\rho_t}{\rho_{182}}$. | r in per cent. Observed | r in per cent. Calculated. |
|---|---|---|---|---|---|
| 35 | ... | ... | ... | 7·2 | ... |
| 100 | ... | ... | ... | 6·2 | ... |
| 182 | 0·95 | 1·00 | 1·00 | 3·5 | 3·2 |
| 204 | 1·56 | 1·64 | 1·48 | 3·4 | 2·8 |
| 228 | 3·00 | 3·15 | 2·25 | 2·5 | 2·2 |
| 247 | 4·9 | 5·14 | 3·00 | 2·0 | 2·0 |
| 267 | 11·9 | 12·5 | 4·5 | 1·5 | 1·2 |
| 280 | ... | ... | ... | 0·9 | ... |

TABLE II.—SCATTERING IN LIQUID BENZENE.

| Temperature. t°c. | $S_t/S_c$ | r Observed. | r Calculated. |
|---|---|---|---|
| 35 | 3·2 | 43 | 44 |
| 125 | 3·67 | 32 | 31 |
| 182 | 5·48 | 19 | 16 |
| 205 | 7·21 | 14 | 10·3 |
| 228 | 11·0 | 9·5 | 7·0 |
| 268 | 20·5 | 3·0 | 2·9 |
| 280 | ... | 2·8 | ... |
| 283 | 102 | ... | ... |

It will be seen that the intensity of scattering in both the saturated vapour and in the liquid increases rapidly with temperature becoming very large as we approach the critical temperature, and that in the case of the vapour, the increase is much more than in proportion of the density. The imperfection of polarisation shows a diminution with increasing temperature tending to a very small value as we approach the critical point. In the last column of the two tables are shown the values of imperfection of polarisation calculated in the manner indicated in the next section.

## 4. *Polarisation of the transversely scattered light.*

The theory of light-scattering by gases consisting of isotropic molecules as developed by the late Lord Rayleigh and the general theory of scattering of fluids as developed by Einstein on the lines of Smoluchowski's work based on the idea of accidental deviations of density in the fluid, predict a perfect polarisation of the light scattered in a direction at right angles to the incident beam. Einstein's expression for the light scattered in a transverse direction by unit volume of a homogeneous fluid is given by

$$\frac{\pi^2}{18} \frac{\mathrm{R\,T\,B}}{\mathrm{N}\,\lambda^4} (\mu^2 - 1)^2 (\mu^2 + 2)^2$$

where T, $\beta$ are the temperature and compressibility of the fluid, R is the gas-constant per gram-molecule, N the Avogadro-number, $\lambda$ is the wave-length of the incident light and $\mu$ is the refractive index of the fluid. This reduces to Rayleigh's law in the case of gases obeying Boyle's law and experiments at Calcutta on a number of substances both in the liquid and vapour states, have established the general validity of this law.

In the case of most media, however, the transversely scattered light is only imperfectly polarised. This imperfection has been attributed to the anisotropy of the molecules and the general case has been

recently discussed by Raman. In such a medium, there is an extra scattering which is for the most part unpolarised, due to the anisotropy of the molecules. If $\Omega_0$ denote the scattering arising from the fluctuatons of density, $4\Omega_1$ the unpolarised scattering arising from molecular anisotropy and $\Omega_2$ the polarised scattering due to the same cause, the ratio of the weak component to the strong in the transversely scattered light is given by

$$r = \frac{2\,\Omega_1}{\Omega_0 + \Omega_2 + 2\,\Omega_1}$$

In the case of a gas obeying Boyle's law $\Omega_2$ has the value $\frac{1}{3}\Omega_1$. The extra contribution from molecular anisotropy leads to an increased scattering in the ratio

$$\frac{6\,(1 + r)}{6 - 7r}$$

We shall assume this to be true generally.

If the molecules have absolutely random orientations, $\Omega_1$ should be proportional to the number of molecules per unit volume. Since in the case of liquids and vapours, on rise of temperature, $\Omega_0$ increases at a much larger rate than the density (in liquid the density actually decreases), the ratio $2\Omega_1 \div (\Omega_0 + \frac{7}{3}\Omega_1)$ should get smaller and smaller and reach a minimum value at the critical point where the value of $\Omega_0$ is a maximum. We can easily deduce a quantitative relation between the intensity of the transversely scattered light and its imperfection of polarisation.

From equation (2), when $\Omega_2 = \frac{1}{3}\Omega_1$,

$$\Omega_0 = \frac{6-7r}{3r}\,\Omega_1$$

and since $\Omega_1 = k\rho$ where $\rho$ is the density of the substance

$$\Omega \;= \frac{6-7r}{3r}\,k\rho$$

and the total scattering

$$S = \Omega_0 + \frac{13}{3}\,\Omega_1$$

$$= \frac{1+r}{r} \,.\; 2k\rho$$

$$\therefore \frac{S}{\rho} \cdot \frac{r}{1+r} = 2k, \textit{ a constant.}$$

In the last column of tables I and II are given the values of $r$ calculated from this relation. The constant $k$ was calculated from the intensity

and polarisation of the transversely scattered light in saturated benzene vapour at room temperature. The imperfection of polarisation was measured in an apparatus similar to that used by Lord Rayleigh, the vapour being illuminated by means of a strong beam of sunlight. The value of $r$ was found to be 7·2 per cent as against Lord Raleigh's value 6 per cent. The intensity at the room temperature was calculated assuming the validity of the Rayleigh law of scattering (to which the Einstein law reduces when the vapour is sufficiently rare) and applying the correction for the admixture with unpolarised light. The agreement between the calculated and observed values is satisfactory.

5. *Calculation of the intensity of the transversely scattered light.*

For calculating the intensity of the transversely scattered light according to the Einstein-Smoluchowski formula, the refractive index and the compressibility of the medium have to be known. The refractive index can be calculated using Lorentz's relation $(\mu^2-1)/(\mu^2+2)\rho = 0{\cdot}3423$ for benzene[1] (for the F line). There are no data for the compressibility of the liquid* or the vapour for the temperatures at which these experiments were made, but the compressibility of the vapour can be calculated from Dietrici's equation of state, viz.,

$$p = \frac{RT}{v-b} e^{-\frac{a}{RTv}} \qquad (5)$$

with an empirical correction which can be determined in the manner described below. From (5)

$$\frac{1}{\beta} = -\left(v\frac{dp}{dv}\right)_t = p\left\{\frac{v}{v-b} - \frac{a}{RTv}\right\}$$

Putting in the values of $a$ and $b$ in terms of the critical constants $b = v_c/2$ and $a/RT = 4b = 2v_c$ this reduces to

$$-\left(v\frac{dp}{dv}\right)_t = p\left\{\frac{2v}{2v-v_c} - \frac{2v_c}{v}\right\} \qquad (6)$$

where $v$ is the specific volume of the saturated vapour and $v_c$ is the critical volume (volume of 1 gram of the substance at the critical point).

To test the applicability of this equation, the values of the compressiblity of the saturated vapours of ether, isopentane and carbon dioxide were calculated and the values compared with the actual values obtained from the isothermal curves. The actual value of the compressibility is found to be larger than that given by equation (6), the ratio of the actual

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[1] Landolt-Bornstein Tabellen, 1912, p. 1031.

* Except for the liquid up to 100°. For this case, the observed values of the scattering agree with the calculated.

compressibility to that derived from (6), lying in the neighbourhood of 1·25 over a large range. This ratio is plotted against the reduced temperatures. The points for the three different substances lie practically on the same curve, and from 0·8 $T/T$ to 0·96 $T/T_c$ the ratio lies near 1·25. In order to calculate the isothermal compressibility of the saturated vapour of a substance for which the necessary isothermal pressure volume data are not available, we may multiply the compressibility given by equation (6) by the corresponding factor obtained from the curve. Calculating in this way, I find that the scattering in benzene vapour at 267°C is 10 times that of liquid ether at 35°, while the observed value is 11·9 times. At other temperatures, the observed values are even higher than the calculated. This may be due either to the inapplicability of the above method of calculating the compressibility, or to the presence of a trace of impurity in the benzene which would give rise to an additional concentration scattering. The writer hopes to repeat the intensity measurements with carefully purified benzene.

This does not, however, in any way invalidate the main conclusion of the paper, namely, the proportionality of the unpolarized part of the scattered light to the density. The theoretical basis for this rests upon the assumption of the random character of the orientation of the molecules and the agreement of the experimental and theoretical values of the imperfection of the polarization supports the assumption. This relation may not be true in the case of all liquids; with liquids whose molecules behave like electrical di-poles, the orientations are certainly not likely to be *at random*. Experiments on the polarization of the transversely scattered light with other liquids and over a large range of temperature are likely to throw light on the mutual influence of molecules in liquids.

In conclusion, I have much pleasure in recording my thanks to Prof. C. V. Raman under whose inspiring guidance the work described above was carried out in the laboratory of the Indian Association for the Cultivation of Science.

210, Bowbazaar Street,
Calcutta,
*6th August* 1922.

## Addendum.

A question has been raised as to the mean wave-length to be adopted in calculations when using composite light like sunlight for scattering experiments. In the above paper, the wave-length of the F line has been adopted. The influence of the wave-length of the incident light enters in two ways: (1) directly in the $\lambda^4$ factor and (2) indirectly through its influence on $\mu$. When comparing two substances as regards their scattering, the effect of the first and dominant factor is identical

in the two cases; that of the second depends on the dispersive power of the two substances. The values of $(\mu^2-1)^2(\mu^2+2)^2$ for liquid benzene and liquid ether at 20° C have been tabulated below:

*Liquid Benzene at 20° C.*

| λ. | C 6,563 A. | D 5,893 A. | F 4,861 A. | G′ 4,340 A. |
|---|---|---|---|---|
| $\mu$ ... .. | 1·4965 | 1·5011 | 1·5133 | 1·5236 |
| $(\mu^2-1)^2(\mu^2+2)^2$ ... | 27·76 | 28·22 | 30·48 | 32·53 |

*Liquid Ether at 20° C.*

| λ. | C 6,563 A. | D 5,893 A. | F 4,861 A. | G′ 4,340 A. |
|---|---|---|---|---|
| $\mu$ ... ... .. | 1·3519 | 1·3538 | 1·3580 | 1·3607 |
| $(\mu^2-1)^2(\mu^2+2)^2$ ... | 10·95 | 10·16 | 10·56 | 10·77 |

In benzene, the more dispersive substance, the difference between adopting the wave-length of the F line and that of the G′ line for example, comes to nearly 6 per cent. At higher temperatures and for the vapor, the effect would be less and when we remember that our standard of comparison, ether, has itself a higher refractive index towards the violet, the difference between adopting the values of $\mu_F$ and $\mu_{G'}$ reduces to 4 per cent.

As regards the intensity of the scattered light in different parts of the spectrum, it will depend partly on the distribution of energy in the incident light and partly on the law of scattering. Adopting Abbot's values for the energy-distribution in sunlight, and assuming that the energy in the scattered light is proportional to $\lambda^{-4}$, the following are the relative values of the scattered energies:

| λ in A. U. | Incident Energy $I$ in Arbitrary Units. | $I\lambda^{-4}$. |
|---|---|---|
| 6,000 ... ... ... ... | 5,050 | 3·9 × $10^{21}$ |
| 5,400 ... ... ... ... | 5,700 | 6·7 ,, |
| 5,200 ... ... ... ... | 5,900 | 8·1 ,, |
| 5,000 ... ... ... ... | 6,080 | 9·7 ,, |
| 4,800 ... ... ... ... | 6,250 | 11·8 ,, |
| 4,400 ... ... ... ... | 5,820 | 15·5 ,, |
| 4,000 ... ... ... ... | 4,350 | 17·0 ,, |
| 3,800 ... ... ... ... | 3,750 | 18·0 ,, |
| 3,500 ... ... ... .. | 2,700 | 18·0 ,, |

The effect of the dispersion of the substance is to increase the relative importance of the radiations of shorter wave-length and more for a substance of larger than for one of smaller dispersion.

We have now to consider the visual effect of the scattered light. For ordinary luminosities, the maximum visual effect is produced by rays in the neighbourhood of 5,500 A: but for the weak luminosities such as we here deal with, owing to the Purkinje effect, the region of maximum sensitiveness is shifted towards the blue, the shift being a function of the luminosity. Taking everything into account, the effective wave-length of the scattered light is probably a little farther on toward the violet than F; but considering the uncertainties in our knowledge of the luminosity-curves for weak illuminations and the smallness of the error when we use *scattered light for comparison*, the error introduced by adopting the wave-length of the F line for the calculations is not of a serious nature.

CALCUTTA,
*November* 28, 1922.

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# ON THE VISUAL AND PHOTOGRAPHIC ALBEDO OF THE EARTH.

BY K. R. RAMANATHAN.

ABSTRACT.

*The visual and photographic albedo of the earth.*—This subject, previously treated by H. N. Russell and C. G. Abbot, is here discussed afresh in the light of Luckiesh's recent measurements of the visual brightness of earth-areas as seen from an aeroplane and Raman's theory of the colour of the sea as originating from the *molecular scattering of light in deep water*. The effects of molecular scattering by the atmosphere and the sea are considered in detail with reference to the spectral distribution of the scattered light. The computed visual albedo comes out to be 0·46 and the photographic 0·58, in close agreement with the astronomical values 0·45 and 0·6, respectively.

## *Introduction.*

A valuable discussion of the photometric measures of the albedo of the earth was put forward by H. N. Russell[1] who came to the conclusion that the visual albedo of the earth according to Bond's definition as deduced from Very's observations of earth-shine on the moon was 0·45 and the photographic albedo was 0·6. Further, Abbot[2] from radiation measurements and a consideration of the physical characteristics of the earth, has computed the total energy albedo to be 0·37. The difference between the visual and photographic albedoes is considerable and it has

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[1] Astrophysical Journal, Vol. 43, p. 173, 1916.
[2] Annals of the Smithsonian Astroph. Observatory 2, 161–163.

been suggested that this is due to the fact that a part of the light diffused out by the earth arises from the molecular scattering of light in the earth's atmosphere. Since the publication of the papers referred to, two investigations have appeared which makes it desirable to consider the problem of the earth's albedo afresh. Luckiesh[1] has published observations made during aeroplane flights of the visual albedo of different kinds of landscape and also inland and oceanic waters. Then again, Abbot in his discussion of the albedo of water-covered areas considered only the reflection of light at the *surface* of the liquid. In reality we have also to consider the important part arising from the diffusion of light entering the water. A theory of the colour of the sea as being due to the molecular scattering of light in deep ocean water has been put forward by C. V. Raman[2] who has also pointed out the importance of the contribution which the scattered light from the sea would make to the albedo of the earth. In this paper, it is proposed to discuss the problem of the albedo taking into account the spectral distribution of the molecular scattered light from the atmosphere and the sea.

We may divide the light going out of the earth into space as arising in the following ways :—

(1) Light molecularly scattered from the atmosphere above the region of dust.

(2) Light scattered by the clouds.

(3) Light scattered from the unclouded portions of the earth in the lower dusty regions of the atmosphere.

(4) Light diffusely reflected from the earth's surface including the oceans.

Of these, the light molecularly scattered from the atmosphere and the sea would be richer in the shorter wave-lengths and hence on the aggregate, the returning light would be bluer than the incident.

*Light molecularly scattered from the atmosphere above the region of dust.*

The discussions by F. E. Fowle[3] and L. V. King[4] of the extensive measurements of atmospheric transparency made by the Smithsonian Observatory have shown that in the region of wave-lengths shorter than $0{\cdot}69\mu$ the loss of light on a clear day above the Mt. Wilson level (1,730 metres) could be accounted for almost entirely by the molecular scattering of light by the atmosphere.* The selective absorption exercised by the oxygen and water-vapour lie entirely in the region of

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[1] Astrophysical Journal, Vol. 49, p. 108, 1919.

[2] Proc. Roy. Soc. April, 1922. See also "Molecular Diffraction of Light" published by the Calcutta University, 1922.

[3] Astrophysical Journal, Vol. 38, p. 393, 1913.

[4] Phil. Trans. Roy. Soc. A, Vol. 212, p. 375, 1913.

* Except for a possible small selective absorption between $0{\cdot}51\mu$ and $0{\cdot}65\mu$.

wave-lengths longer than $0{\cdot}70\mu$ and hence outside the visual and photographic regions. We shall take Mt. Wilson level to be the upper limit of the region of dust. Abbot has given a table of intensities of energy in the normal solar spectrum outside the earth's atmosphere. From these and the values of the yearly mean dry-air transmission coefficients at Mt. Wilson[1] we can determine graphically from the areas of the energy-wave-length curve the percentage of light lost in transmission in different regions of the spectrum. Between $0{\cdot}45\mu$ and $0{\cdot}68\mu$ which we may take to be the effective visual region, I find the percentage of energy lost on normal transmission to be 10 and in the region between $0{\cdot}35\mu$ and $0{\cdot}45\mu$ which we may take to be the effective photographic region, the percentage is 24. We have now to consider the actual loss that occurs taking into account the facts that at a large portion of the earth's surface, the light is incident obliquely and that on the average, a portion of the atmosphere above Mt. Wilson level is always clouded. At the place where the sun's rays meet the earth at an angle $i$, the transmission coefficient is $a^{\sec i}$ where $a$ denotes the same quantity for normal incidence. The quantity of light falling on the surface of a sphere of radius $r$ between the angles $i$ and $i+di$ is

$$2\,\pi\,r^2\,\mathrm{I}\sin i\cos i\,di$$

where I is the intensity of the incident light. The amount of light transmitted in the same range is

$$2\pi\,r^2\,\mathrm{I}\sin i\cos i\,a^{\sec i}\,di$$

and this, taken over the whole sphere is.

$$2\pi\,r^2\,\mathrm{I}\int_0^{\pi/2}\sin i\cos i\,a^{\sec i}\,di$$

The integral does not seem to be capable of being easily evaluated; instead, it was done by graphical integration and the total loss in the visual region was found to be 17 per cent and in the photographic region 38 per cent. Assuming that half this amount would be reflected back to space, we get $8{\cdot}5$ per cent to be the visual and 19 per cent to be the photographic albedoes of the atmosphere above Mt. Wilson if it were entirely unclouded. Actually, however, according to Abbot,[2] about 60 per cent of the earth's cloudiness is above Mt. Wilson level and since, on the average, 52 per cent of the earth's surface is always clouded, 31 per cent of the skies above Mt. Wilson will be always covered by clouds. The distribution of clouds with height as given in Humphreys' "Physics of the Air" [1] is as follows :—

1. Cirrus level : height above surface about 10 km.
2. Cirro-stratus level : height above surface about 8 km.

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[1] Fowler : Smithsonian Misc. Collections, Vol. 69, No. 3.
[2] Page 309.

3. Alto-cumulus level : height above surface about 4 km.
4. Cumulus level : height above surface about 1·5 km.
5. Fog-level : ground.

Of these, the first two would be comparatively thin and would transmit a large portion of the light. We may take the average cloud-height above Mt. Wilson to be $5\frac{1}{2}$ km. corresponding to a level at which the pressure is half the sea-level pressure. Thus the albedo due to the molecular scattering of the atmosphere above the dust-level would be

TABLE I

| | Visual | Photographic |
|---|---|---|
| From cloudless portion ... | $0{\cdot}69 \times 8{\cdot}5$ | $0{\cdot}69 \times 19$ |
| From clouded portion ... | $0{\cdot}31 \times \frac{38}{63} \times 8{\cdot}5$ | $0{\cdot}31 \times \frac{38}{63} \times 85$ |
| Total ... | 7·5 per cent | 1·7per cent |

We have assumed the fraction scattered from the clouded portion to be less than that from the unclouded in the ratio of the pressure above the average higher cloud-level to the pressure at Mt. Wilson. We have also neglected the scattering due to the moisture in the dustless region

*Light reflected from the clouds.*

According to Abbot's energy-measurements and Luckiesh's photo metric observations, we shall take the average reflecting power of clouds to be 65 per cent. Since the average cloudiness of the earth is 52 per cent we get for the percentage of light reflected back from the clouds the values given in Table II.

Table II.

| | Visual. | | Photographic. | |
|---|---|---|---|---|
| | Percentage incident | Percentage reflected | Percentage incident | Percentage reflected |
| From higher clouds (average level $5\frac{1}{2}$ km) | $100 - \frac{38}{63} \times 8{\cdot}5 = 95$ | $0{\cdot}31 \times 95 \times 0{\cdot}65 = 19{\cdot}1$ | $100 - \frac{38}{63} \times 19 = 88{\cdot}6$ | $0{\cdot}31 \times 88{\cdot}6 \times 0{\cdot}65 = 17{\cdot}9$ |
| From lower clouds (average level 1·7 km). | $100 - 8{\cdot}5 = 91{\cdot}5$ | $0{\cdot}21 \times 91{\cdot}5 \times 0{\cdot}65 = 12{\cdot}5$ | $100 - 19 = 81$ | $0{\cdot}21 \times 81 \times 0{\cdot}65 = 11{\cdot}1$ |
| Total .. | ... | 31·6 | ... | 29·0 |

Very little need be allowed from this for loss in transmission upward, for the diminution is due to scattering and the scattered light would either go up or again get reflected from the clouds.

*Light scattered from the lower atmosphere.*

The light reflected from the lowor atmosphere below the Mt. Wilson level can be calculated as follows. From Abbot's data[1] for the mean coefficients of normal atmospheric transmission at Mt. Wilson and Washington, the percentage of energy lost between the levels of the two stations is calculated for different wave-lengths, and an energy-wave-length curve constructed with these data. From the area of the curve, it is found that in the region $0{\cdot}45\mu$–$0{\cdot}68\mu$, 14 per cent of the energy is lost, and practically the same percentage between $0{\cdot}35\mu$ and $0{\cdot}45\mu$. Assuming 20 per cent of this to be absorbed, and half the remainder to be sent to earth and the other half back, we get 6 per cent to be the ratio of the light reflected back at normal incidence. Taking into account the facts that at a considerable portion of the earth, the light is incident obliquely and that only 48 per cent of the earth is unclouded, the contribution of the lower atmosphere comes out to be nearly 4·5 per cent.

The above estimates agree very well with the careful visual photometric measurements of Kimball[2] who found a mean transmission coefficient of 0·77 in clear weather corresponding to the estimate here made of a loss of 10 per cent above Mt. Wilson and 14 per cent below it.

*Light reflected from the Earth's surface.*

Since more than three-fourths of the earth's surface is covered by seas, the most important contribution of the albedo from the surface of the earth would come from them. The deep-blue colour of the ocean waters has been explained by C. V. Raman[3] as originating from the molecular scattering of light within the water. The fraction of the incident energy scattered by unit volume of a homogeneous fluid like water is for the most part given by the Einstein-Smoluchowski expression.

$$\frac{8\pi^3}{27}\,\frac{RT\beta}{N\lambda^4}\,(\mu^2-1)^2\,(\mu^2+2)^2, \qquad (2)$$

where $\beta$ is the isothermal compressibility of the medium, $\mu$ its refractive index, N the Avogadro constant and $\lambda$ the wave-length of the incident light. R and T have their usual meanings in the kinetic theory. Since the amount of scattered light varies inversely as the fourth power of the wave-length, we can easily see why the blue end of the spectrum should predominate in the light returning from the water. Two other factors go to make scattered light even a richer blue : one is the greater absorption in water of the red and yellow regions of the

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[1] Astroph. Journal, Vol. 34, p. 203, 1911.
[2] Monthly Weather Review 43, 650, 1914 also H. N. Russell's article, loc. cit.
[3] Proc. Roy. Soc. A. 101, 64, 1922.

spectrum and the other is an addition to the light scattered in accordance with (2), of some unpolarised light which is greater in the violet end of the spectrum.[1] In his paper, Raman has given a table of the luminosity of deep ocean water for different wave-lengths in terms of the luminosity of a layer of dust-free air one kilometre thick when viewed transversely to the incident light. In calculating these values, he made use of the absorption co-efficients of water obtained by Count Aufsess. Recently W. H. Martin[2] has obtained fresh values for the absorption co-efficients with pure dust-free water and the following table gives Raman's revised values for the luminosity of ocean water in terms of that of an atmosphere of dust-free air which would give an equal effect by lateral scattering.

TABLE III.—*Luminosity of ocean water.*

| Wave-length in $\mu$ .. | 0·658 | 0·602 | 0·590 | 0·578 | 0·546 | 0·499 | 0·436 |
|---|---|---|---|---|---|---|---|
| Equivalent atmospheres of dust-free air. | 0·06 | 0·09 | 0·23 | 0·35 | 0·65 | 0·90 | 2·0 |

Confining ourselves to the region 0·45 to 0·68 $\mu$, the fraction of incident light scattered comes out to be ·06. Luckiesh's direct determination of the "reflecting" power of the Atlantic as measured from an aeroplane gave an average value of 3·5 per cent. The difference is no doubt to be attributed to the fact that in the above calculation, the absorption co-efficient has been assumed to be equal to that of dust-free distilled water. Luckiesh makes it clear that 90 per cent of the light returning from the sea as viewed normally is due to light diffused within it. The above estimate refers to direct overhead observation. In an oblique direction the molecular scattering would give rise to a greater luminosity as a more extensive surface layer of water would come into operation, and indeed, Luckiesh has noticed that the brightness increases more than twice when the sea-surface is viewed at an angle of 45°.

Besides the molecular scattering, there is also the specular reflexion to be taken into account which would give rise to a reflection factor of about 3 per cent.

On the whole, we may put 8 per cent to be the fraction coming back from the ocean waters. As regards land areas, Luckiesh has obtained the following reflection factors for some typical surfaces :—

| Fields. | Barren lands. | Woods. |
|---|---|---|
| 7·2 | 12·0 | 4·3 per cent. |

[1]. C. V. Raman, "Molecular Scattering of Light," page 55.
[2]. Journal of Phys. Chemistry, May 1922.

A snow covered surface is known to reflect about 75 per cent. of the incident light, but almost the whole of the snow-covered areas of the earth are near the poles where only a small fraction of the sun's energy is received and where, moreover, a large part of the incident light would have been scattered by the atmosphere before reaching the earth. We may take, without much error 12 per cent. to be the average reflecting power of the land areas of the earth. Thus, the percentage of light scattered from the earth surface in the visual region would come to be nearly 0·80 ($\frac{3}{4}\times 8+\frac{1}{4}\times 12$), i.e., 7·2. Of this, allowing 30 per cent. for loss on transmission through the atmosphere and remembering that only 48 per cent. of the earth's surface is unclouded, we get 2·5 per cent. to be the contribution of the surface of the earth to the visual albedo.

As regards the photographic albedo, the scattered light from the sea would contribute much more. An examination of the table given above would show the enormous concentration of energy in the violet end of the spectrum. In the near ultra-violet, the light scattered from the sea is likely to be even stronger, since the absorption-co-efficient of water gets smaller and smaller as we go to the region of shorter wave-lengths. But against this, it has to be said that the presence of motes would tend to increase the absorption. We have previously estimated the photographic albedo of the sky above Mt. Wilson to be 0·19, and from the table it is evident that we would not be far wrong if we take the fraction of the incident energy scattered by the sea to be 0·30. With the usual allowance for the loss of energy of the incident and reflected rays on transmission through the atmosphere and the fact that a portion of the earth's surface is clouded, we get the photagraphic albedo due to the sea to be nearly 6 per cent. The land areas would contribute practically nothing to the photographic albedo except the snowy regions near the poles whose effect may come to about 1 per cent. Thus, the aggregate photographic albedo due to the surface of the earth would come to nearly 7 per cent.

TABLE IV.—*Summary.*

| | Visual. | Photographic. |
|---|---|---|
| | PER CENT. | PER CENT. |
| Light scattered from the gases of the atmosphere above the dust. | 7·5 | 17 |
| Light reflected from the clouds ... | 31·6 | 29·0 |
| Light scattered from the lower atmosphere. | 4·5 | 4·5 |
| Light reflected from the surface of the earth including the oceans | 2·5 | 7 0 |
| Total ... | 46 | 57·5 |

The visual and photographic albedoes obtained above agree very well with the astronomical values 0·45 and 0·6. Considering the uncertainties

in the estimation of the earth's albedo factors and the difficulties of photometric measurement of the earth-shine on the moon, the agreement is actually better than could have been anticipated.

In conclusion, I have great pleasure in expressing my thanks to Professor C. V. Raman for his suggestion of the problem and interest in the progress of the work.

UNIVERSITY COLLEGE,
RANGOON,
*5th August* 1922.

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# ON THE COLOUR OF THE SEA.

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## 1. *Introduction.*

In a recent paper[1], Prof. C. V. Raman has put forward the theory that the deep blue colour characteristic of the larger part of ocean waters is due to the molecular scattering of light in water and supported it by calculations of the intensity and quality of the light returned from deep water. He has shown that pure, dust free water scatters light in accordance with a formula originally deduced by Einstein for the critical opalescence of fluids and that molecular scattering by itself without the aid of any extraneous agency is sufficient to account for the return of a part of the incident light. The following investigation was undertaken in order to test how far actual sea-water comes up to the ideal dust-free condition, and to find how the waters in seas showing different colours vary from one another.

## 2. *Theoretical Discussion.*

Preliminarily, it is useful to consider what intensity and colour we should expect from a perfectly *absorption-less* dust free ocean of infinite depth. In such a case, the diminution of intensity of light in its passage through the medium would be wholly accounted for by molecular scattering. Since there is no transformation of the incident energy, it would be entirely thrown back, and the returned light would be of the same quality as the incident.[2] Since the scattering co-efficient varies inversely as the fourth-power of the wave-length, the depth of the medium responsible for the return of a certain percentage of blue

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[1] C. V. Raman, Proc. Roy. Soc. A, Vol. 101, 1922, p. 64. See also "Molecular Diffraction of Light," Calcutta University Press, 1922, Chapter V.

[2] Vide Schuster, Theory of Optics, Second Edition, p. 271,

light would be smaller than that responsible for the return of the same percentage of red light. Selective absorption however would modify the condition of affairs. The light of those wave-lengths for which the medium exercises a selective absorption would be gradually diminished in intensity as the light penetrates into the medium, and if the absorption is at all considerable, there would be very little of these radiations returned. Now, water is known to exercise a selective absorption in the red which gradually decreases as we proceed into the region of shorter wave-lengths. The most extensive measurements of absorption co-efficients for water that we possess are those of Count Aufsess[1] between wave-lengths 658 $\mu\mu$ and 494 $\mu\mu$. Recently, W. H. Martin[2] has measured the absorption co-efficients of water repeatedly distilled in vacuo for the mercury lines 578 $\mu\mu$, 546·1 $\mu\mu$ and 435·8 $\mu\mu$. As has been pointed out by Martin, there is an error in Aufsess's measurements as he neglected to take into account the loss of light on reflection at the glass surfaces at the ends of the absorption tube. However, considering the length of tube which Aufsess employed (5·5 metres), the relative error involved is not large in the region of the red where the absorption is large. We shall therefore adopt Aufsess's values for the absorption co-efficients in the red. In the following table are shown the experimental values of the extinction co-efficient $\gamma$ defined by $I = I_o e^{-\gamma x}$ where $I_o$ is the intensity of a parallel beam of incident light and I is the intensity after traversing a thickness $x$ of water. In the fourth column are shown the values of the extinction co-efficients if the extinction were due *solely* to molecular scattering. These are calculated according to the formula.

$$\gamma = \frac{8\pi^3}{27} \frac{RT\beta}{N\lambda^4}. (\mu^2-1)^2 (\mu^2+2)^2.^{*}$$

[1] Count Aufsess Ann. der Physik, Vol. 13, 1904.

[2] W. H. Martin : Journal of Phys. Chem. 26, 1922, p. 471.

* Vide C. V. Raman, loc. cit. and "Molecular Diffraction of Light", Chapter IV, p. 52.

This is derived on the assumption that the light scattered in a direction perpendicular to the incident beam is perfectly polarized. As a matter of fact the transversely scattered light shows defect in polarization. In addition to the polarized "Einstein scattering," there is an additional scattering due to the anisotropy of the molecules, which for the most part is unpolarized. If we take the latter also into account, the formula for the co-efficient of extinction becomes

$$\gamma = \frac{8\pi^3}{27} \frac{RT\beta}{N\lambda^4} (\mu^2-1)^2 (\mu^2+2)^2 \left(\frac{6+3r}{6-7r}\right)$$

where $r$ is the ratio of the weak component to the strong in the transversely scattered light, and the values of the extinction co-efficients come out to be $8{\cdot}9 \times 10^{-6}$, $1{\cdot}2 \times 10^{-5}$, $1{\cdot}55 \times 10^{-5}$, $1{\cdot}9 \times 10^{-5}$, and $5{\cdot}2 \times 10^{-5}$, for the wave lengths given above.

TABLE I.

| Wave-length. | Absorption co-efficient. | Author. | Extinction co-efficient due to scattering alone. |
|---|---|---|---|
| 658 ... ... ... .. | $3{\cdot}2 \times 10^{-3}$ | Aufsess. | $7{\cdot}5 \times 10^{-6}$ |
| 612 ... ... ... .. | $2{\cdot}33 \times 10^{-3}$ | Aufsess. | $9{\cdot}9 \times 10^{-6}$ |
| 578 ... ... ... ... | $6{\cdot}4 \times 10^{-4}$ | Martin. | $1{\cdot}3 \times 10^{-5}$ |
| 546·1 ... ... ... ... | $3{\cdot}4 \times 10^{-4}$ | Martin. | $1{\cdot}6 \times 10^{-5}$ |
| 435·8 ... ... ... ... | $1{\cdot}2 \times 10^{-4}$ | Martin. | $4{\cdot}3 \times 10^{-5}$ |

In the red, yellow and green up to 546 $\mu\mu$, practically the whole of the extinction is due to absorption, while in the blue and the violet, scattering takes away an appreciable part. The intensity of the incident radiation is reduced to one-half at a depth of approximately 2 metres for 658 $\mu\mu$, 10 metres for 578 $\mu\mu$, 20 metres for 546 $\mu\mu$ and 60 metres for 435 $\mu\mu$. Taking primary scattering alone into account and considering the directions of incidence and observation to be vertical, the total observed brightness due to an infinite depth of water can be easily shown to be $B/\gamma\lambda^4$, where the scattering co-efficient in a transverse direction has the value

$$\frac{\pi^2}{18}\frac{RT\delta}{N\lambda^4}(\mu^2-1)^2(\mu^2+2)^2.$$

We can now see why the returned light should be specially deficient in the red, yellow and green. The increase in absorption goes hand in hand with the decrease in scattering and the two together serve practically to eliminate the longer wave-lengths. The following table gives the course of values of $B/\gamma\lambda^4$ :—

| $\lambda$ in $\mu\mu$ | 658. | 612. | 578. | 546. | 436. |
|---|---|---|---|---|---|
| $B/\gamma\lambda^4$ ... ... | $1{\cdot}4 \times 10^{-4}$ | $2{\cdot}5 \times 10^{-4}$ | $1{\cdot}2 \times 10^{-3}$ | $2{\cdot}8 \times 10^{-3}$ | $2{\cdot}1 \times 10^{-2}$ |

In order to obtain the resultant colour of the sea, we have only to compound the effects of different wave-lengths in their proper proportions. The intensities for the different wave-lengths throughout the visible spectrum can be obtained by the above formula and their colour effects expressed in terms of the spectrum colours 630·2 $\mu\mu$ 538·1 $\mu\mu$ and 456·9 $\mu\mu$ using the values given by the late Lord Rayleigh in his paper on "The Colours of Thin Plates."[2] The resultant colour is found to have the composition $1{\cdot}56\times10^{-3}$ red, $2{\cdot}49\times10^{-2}$ green and $9{\cdot}53\times10^{-2}$

[1] C. V. Raman, *loc cit.* If the anisotropic scattering is also taken into account, this would become $B(1+r)/\gamma\lambda^4$.

[2] Lord Rayleigh, Scientific Papers, Vol. II, Table 1, p. 503.

violet and approaches the spectrum colour 475·0 $\mu\mu$, being very near the indigo of the second order in the colours of thin plates. The inclusion of secondary scattering would reduce the effective depth of the sea from which the scattered light returns ; it would also serve to further diminish the intensities of the red and yellow for which the absorption is strong.

It is obvious that the presence of any dissolved matter giving rise to extra absorption in any particular region of the spectrum would cause a corresponding diminition of the intensity of the returning light in that region of the spectrum.

Let us now consider the effect of suspended matter. It would give rise to an additional scattering and hence the depth to which the light would penetrate would get reduced. If the particles are small in comparison with the wave-length, the scattering would still be proportional to $\lambda^{-4}$. If present in small quantities, there would be little effect on the character of the returned light, but if present in larger quantities, there would be less chance for the absorptive properties of the medium to have their full play and as a consequence, the light would be more mixed with the longer wave-lengths and the blue colour of the sea would tend to get less saturated. As the particles get larger in comparison with the wave-length, the scattering in the direction of primary propagation will be specially favoured and also instead of being proportional to it would tend to be independent of the wave-length. Since the light of longer wave-lengths can return by other means than molecular scattering, their relative proportion in the light returned would increase more and more as the quantity of suspended matter increases, and the sea would get greenish blue, green, whitish green and finally white. However, as we shall see, when the quantity of matter is not large, the light scattered against the direction of the incident light is but an insignificant fraction of that scattered in the direction of the incident light.

### 3. *Examination of light scattered by sea water.*

Samples of sea-water were collected in carefully cleaned stoppered bottles from the Bay of Bengal in two voyages between Calcutta and Rangoon from places where the sea exhibited different colours varying from deep indigo to green. The bottles were securely placed in a galvanized iron wire cage tied to the end of wire and the cage was thrown into the sea from the lower deck of the ship near the bow The bottles were rinsed out with the sea-water five or six times before each sample was finally collected. The colour of the sea at the time was also noted. In observing the proper colour of the sea, a nicol is helpful in abolishing sky-reflection, as has been pointed out by Raman.

The scattering of light by the different specimens was examined by concentrating a beam of sunlight at the centre of each bottle in a dark room. The back surfaces of the bottles were painted black in order to

be better able to see the tracks. The following table gives the details regarding the scattering in different specimens. The intensities of the transversely scattered light given in the last column are expressed in terms of that in dust-free distilled water.

TABLE II.

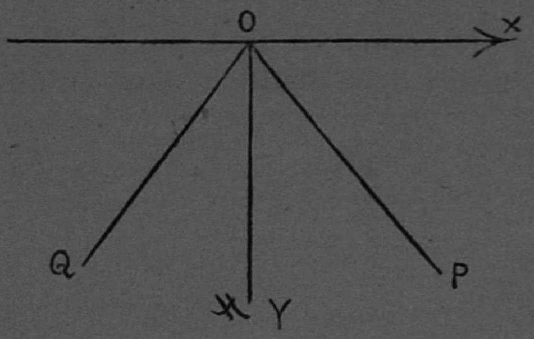
| Specimen number. | Date and time of collection. | Approximate position of ship at time of collection. | Colour of sea. | Appearance of transversely scattered light. | Intensity of transversely scattered light. |
|---|---|---|---|---|---|
| A | 1st October 1922, 10-30 a.m. | ...... | Indigo ... | Indigo with visible particles. | 1·68 |
| B | 4th November 1922, 8 a.m. | Lat. 19° 40′ N Long. 90° E. | Greenish blue. | Blue-Few visible particles. | 1·4 |
| C | 4th November 1922, 11-15 a.m. | Lat. 19° 10′ N Long. 90° 30′ E. | Deep blue. | Indigo—A few large particles. | 1·5 |
| D | 4th November 1922, 4 p.m. | Lat. 18° 30′ N Long. 91° E. | Indigo ... | Do. | 1·5 |
| E | 5th November 1922, 7-30 a.m. | ...... | Greenish ... | Blue with large thin flakes of something floating. | 1·65 |
| F | 5th November 1922, 11 40 a.m. | Lat. 15° 30′ N Long. 94° 15′ E. | Green ... | Bluish white motes visible. | 1·6 Blue. 2·0 Red. |

The colour of the transversely scattered light in specimens A, C and D approached that of dust-free distilled water. The intensity of the transversely scattered light from A was compared with that from dust-free distilled water by sending a concentrated beam of light through the two bottles in succession and making use of an Abney rotating disc photometer for equalizing the intensities. Correction was made for the loss of light on reflection at the glass surfaces. In the case of the other specimens, the comparisons were made by inserting perpendicularly in the path of the stronger beam a number of thin selected microscope slides so as to equalize the apparent brightnesses.

When the direction of observation was OP instead of OY, the suspended particles were much more in evidence and the colour was more reddish. On the other hand, in the direction OQ, the particles were less conspicuous and the colour even more saturated than along OY. This is what we should expect if the particles are large in comparison with the

wave-length. Since in the case of the sea, we are primarily concerned with the light proceeding backward, we should consider the intensity

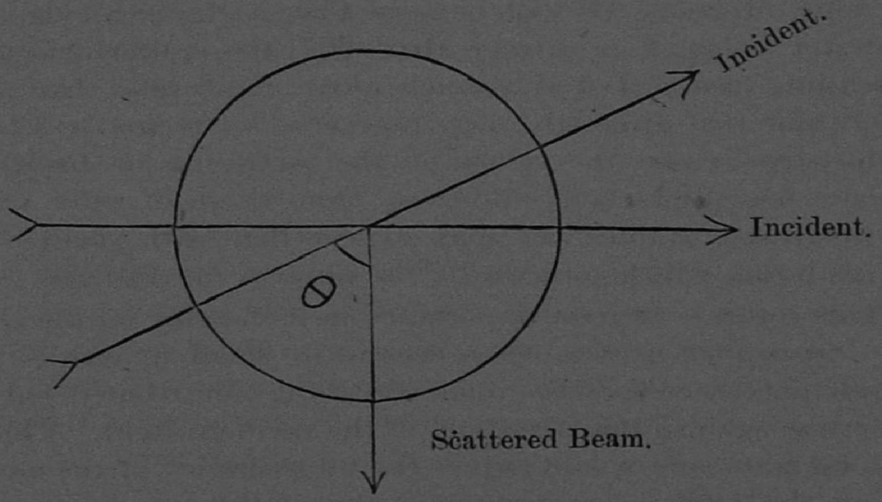
FIG. I.




of the scattered beam in a direction against that of the incident beam. Comparisons of the intensity of scattering in different directions were made by the method indicated below (Fig. 2).

Two beams of sunlight were concentrated one above the other at the centre of the bottle by two lenses of the same focal length (nearly 100 cm. and achromatic) in directions making a definite angle with each other. The scattering was observed in a direction at right angles to one

FIG. II.




of the beams and the apertures of the lenses were adjusted by suitable shutters so that the tracks appeared of equal intensity. The inverse ratio of the areas of the apertures gives the ratio of the intensities scattered in two directions. Since the depth of layer contributing to the luminosity is different in the two cases, being proportional to cosec $\theta$ where $\theta$ is the angle indicated in the figure, the luminosity observed in the direction $\theta$ was multiplied by sin $\theta$ in order to get the

effect due to the same thickness of radiating column. The following table gives the relative intensities of scattering in different directions in specimen A.

### TABLE III.

$S_\theta$—Scattering in specimen in direction $\theta$.
$\sigma_\theta$—Scattering in dust-free distilled water in direction $\theta$.

| $\theta$. | $S_\theta/S_{90°}$. | $S_\theta/\sigma_{90°}$. | $\sigma_\theta/\sigma_{90°}$. |
|---|---|---|---|
| 30° | 1·12 | 1·88 | 1·60 |
| 45° | 0·91 | 1·53 | 1·40 |
| 60° | 0·87 | 1·46 | 1·20 |
| 90° | 1·00 | 1·68 | 1·00 |
| 120° | 2·54 | 4·26 | 1·20 |
| 150° | 5·5 | 9·2 | 1·60 |

The values in the fourth column are calculated on the assumption that the scattering by a pure, dust-free liquid in a direction $\theta$ is given by $\sigma\left(1+\frac{1-r}{1+r}\cos^2\theta\right)$, where $\sigma$ is the scattering in a direction perpendicular to the incident beam and $r$ is the imperfection of polarization in the same direction. It will be seen that in the particular specimen of sea-water, when $\theta$ is greater than 90°, the scattering increases with increasing values of $\theta$ at a much more rapid rate than in dust-free water, and that although the transverse scattering is 1·68 times that of dust-free water, the values of the scattering in directions 30° and 45° are not appreciably different from those of pure water. From the progress of values, we may expect that with smaller values of $\theta$, the scattering will be practically the same as for dust-free water.

This result is of great importance in its bearing on the colour of the sea. Suspended matter, when present in small quantities, although it considerably increases the total scattering contributes but little to the scattering against the direction of the incident light. The increase in the total scattering would reduce the transparency of the medium, but so long as the defect of transparency due to this cause is small compared to the absorption proper, the quality and intensity of the returned light would not be much affected by the presence of such matter.

The following table gives similar data for specimens B, C and F. With a view to bring out the difference in the distribution of scattered light for red and blue, comparisons were made after introducing ruby-red and deep-blue glasses respectively in the paths of the scattered beams.

*Table IV.*

| θ | $S_\theta / S_{90^\circ}$ | | | | | |
|---|---|---|---|---|---|---|
| | B | | C | | F | |
| | Red. | Blue. | Red. | Blue. | Red. | Blue. |
| 30° | 1·01 | 1·22 | 1·06 | 1·13 | 0·88 | 1·03 |
| 45° | 1·10 | 1·05 | 1·13 | 1·13 | 0·95 | 1·02 |
| 60° | 0·90 | 1·00 | 0·97 | 0·97 | 0·83 | 0·95 |
| 90° | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 |
| 120° | 1·65 | 1·52 | 1·55 | 1.60 | 2·09 | 1·63 |
| 135° | 3·92 | 2·45 | 3·18 | 2·76 | 5·05 | 3·98 |
| 150° | 9·0 | 6·0 | 8·3 | 6·3 | 16 | 9·4 |

It will be observed that in all cases, the red gets more and more prominent as θ increases.

We shall now examine whether we can find in the varying amount of suspended matter a sufficient cause for the difference in the colour of the seas. For example, the specimen C was collected from a deep blue sea, while specimen B was from a sea which showed greenish blue and F from a place where the sea was green. Compared with C, the intensity of scattering in F, although nearly equal for the blue in a transverse direction, is greater by 30 per cent in the red and the asymmetry of scattering also is greater. Thus, the total scattering by a unit volume of specimen F is greater than that of C and the colour is also much less blue. Both these causes would contribute to a less deep penetration of the light into the medium (relatively more so for the longer wave-lengths) and thus the absorption would have less chance of playing its full role, so that the blue, indigo and violet would be mixed up with a greater proportion of the longer wave-lengths. We should therefore expect the sea to be brighter and of a less saturated blue, but not the distinct green that it actually was. We have therefore to look for some other cause for the green colour. The point is even clearer if we compare the behaviour of B and C, B scatters actually less than C in a transverse direction (nearly 10 per cent less) and although its track was not indigo like that of C, the asymmetry of scattering was of practically the same order of quantities and yet the colour of the sea from which it was collected was *greenish blue.*

## *IV. Fluorescence of Sea-Water.*

The reason for the difference was found on examining the transversely scattered light from a horizontal track for polarisation by means of a double-image prism. When the double-image prism is so oriented as to transmit vertical and horizontal vibrations, the light corresponding to the horizontal vibrations do not actually vanish even in the case of dust-free

distilled water,[1] but in this case, the two beams are of practically the same colour, while in the case of specimens B and F, the weaker component was found to be distinctly greenish. The contrast came out sharper when the two beams were equalized for brightness by means of a suitably oriented nicol placed behind the double-image prism and a double thickness of blue glass was introduced in the path of the incident beam. The green was now much brighter than the blue and the colour contrast sharper. This was evidently a case of *fluorescence.*

To make quite sure, the following arrangement was adopted. In the path of the incident beam was placed a double thickness of cobalt blue glass with an absorption cell of a solution of potassium permanganate which cut off everything except the extreme blue and violet and a patch in the extreme red. The light was then passed through the sea-water and the track therein was examined through a prism with its refracting edge horizontal. In addition to the blue and violet, the green was also conspicuously present. Yellow and red were present but were very faint. Specimen F showed the effect best, B and E came next and then C and D. The fluorescence was certainly present even in the last two specimens though it was very weak.

Since the incident light did not contain any ultra-violet, the fluorescence should have been excited by the blue and violet. This implies an extra absorption of the blue and the violet. A sea whose water shows the fluorescence would thus appear green not only because there is a return of green light due to fluorescence, but also there would be less of the blue and violet returning. As we have seen, that water looks most green which shows the most intense fluorescence and the water gets more and more towards indigo as the fluorescent material present gets less and less.

The transition from the indigo of the deep sea far from land to blue and green may thus be due either to the increase in the amount of suspended matter present or to the presence of some fluorescent material (most probably organic) which not only causes a return of the green and longer wave-lengths, but also produces a greater absorption of the blue and the violet. The second cause is apparently the more important.

## *V. Summary.*

The paper contains a discussion of the origin of the colour of the sea with observations on the scattering of light by different specimens of sea water from the Bay of Bengal.

(i) It is shown that an ocean of pure, dust-free water would, owing to the effects of molecular scattering and absorption return light of an indigo-blue colour. The presence of *small* quantities of suspended

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[1] W. H. Martin—Journ. Phys. Chem., Vol. 24, 1920, p. 478.
C. V. Raman—"Molecular Diffraction of Light", Chap. IV.

matter would not appreciably affect the colour. With increasing quantities of suspended matter, the colour would change to bluish-green, green, greenish white and white.

(ii) The transverse scattering from different specimens of sea-water has been compared with that of dust-free vacuum-distilled water. The water from the deep blue sea scatters light of nearly the same colour as dust-free water and the intensity of the transversely scattered light is also of the same order.

(iii) The intensity of scattering in different directions from different specimens of sea-water has been studied. The effect of dust is negligible so far as scattering against the direction of the incident light is concerned.

(iv) The variation of the dust-content is found to be insufficient to explain the changes of the colour of the sea from place to place. An important reason for the colour changes has been traced to the presence of varying amounts of some fluorescent material present in the sea. It is pointed out that this fluorescence also implies a greater absorption in the blue and violet involving a diminution of intensity at this end of the spectrum in the light returned from the sea.

In conclusion, I would express my most sincere thanks to Professor C. V. Raman for his stimulating interest in the work.

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# THE MOLECULAR SCATTERING OF LIGHT IN CARBON-DIOXIDE AT HIGH PRESSURES.

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## 1. *Introduction.*

The investigation described in this paper was undertaken in order to test theories of light-scattering by quantitative observations on carbon-dioxide under pressures ranging from 1 to 100 atmospheres, and temperatures from 0° C to 50° C. The work includes a study of the following cases : (1) the scattering of light by the unsaturated vapour ; (2) by the saturated vapour in thermal equilibrium with the liquid ; (3) by the liquid under the pressure of its own vapour ; (4) by the liquid under impressed pressure higher than the vapour tension ; (5) by the substance in the vicinity of the critical state ; and (6) by the substance

in the gaseous state above the critical temperature.* Carbon-dioxide was chosen as a suitable substance for a comprehensive study of this kind for several reasons. The fact that it can be obtained commercially in cylinders in a practically pure condition greatly simplifies the experimental technique, and any pressure within the limits mentioned can be obtained without the use of special compressors. Then again the necessary pressure-volume data for the vapour and the gas are available from the work of Amagat[1] and for the liquid from that of Jenkin[2] and the variation of its refractive index with density has also been fully studied by various investigators, notably by Phillips[3]. The existence of these data makes a theoretical calculation of the light-scattering possible. Further, carbon dioxide at atmospheric pressure shows a marked imperfection in the polarization of the transversely scattered light, the ratio of the weak to the strong component of polarization in the visual region of the spectrum being 10·6 per cent. Hence it is a very convenient substance for studying the effect of variations of temperature and pressure on the state of polarization of the scattered light.

Another reason why we felt impelled to take up a careful study of the scattering of light in carbon-dioxide was that certain results obtained by Lord Rayleigh with this gas[4] were as has already been pointed out by us†, anomalous and stood in need of explanation. Rayleigh determined the intensity of the light scattered by carbon dioxide vapour contained in a steel cross-tube provided with glass windows and kept in communication with a steel cylinder containing liquid $CO_2$ at 21° C. He found the scattering to be 102 times stronger than that of $CO_2$ at atmospheric pressure and inferred that the scattering power was proportional to the density within the limits of experimental error. According to the Einstein-Smoluchowski formula, however, the scattering power should have been much larger, about 800 times that of $CO_2$ at atmospheric pressure. With regard to this discrepancy, it should be mentioned that Rayleigh's assumption that the density of the gas in his observation tube was equal to that of the saturated vapour at 21° C, is open to question. It is mentioned in his paper that the observation tube was leaky and that a gauge in the communication tube from the supply cylinder indicated only 50 atmospheres while according to the measurements of Andrews, the saturation pressure at 21° C is 60 atmospheres. From the diagram given in Rayleigh's paper, it is noticed that after passing the pressure gauge the gas had to filter through a

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* The cases in which the fluid is superheated or supercooled and is in metastable equilibrium are not dealt with here.

1. Amagat—Ann. Chem. Phys. (6) 29, p. 52 (1893).
2. Jenkin—Proc. Roy. Soc. A, Vol. 98, p. 170.
3. Phillips—Proc. Roy. Soc. A, Vol. 97, p. 225.
4. Lord Rayleigh—Proc. Roy. Soc. A, Vol. 95, p. 155.

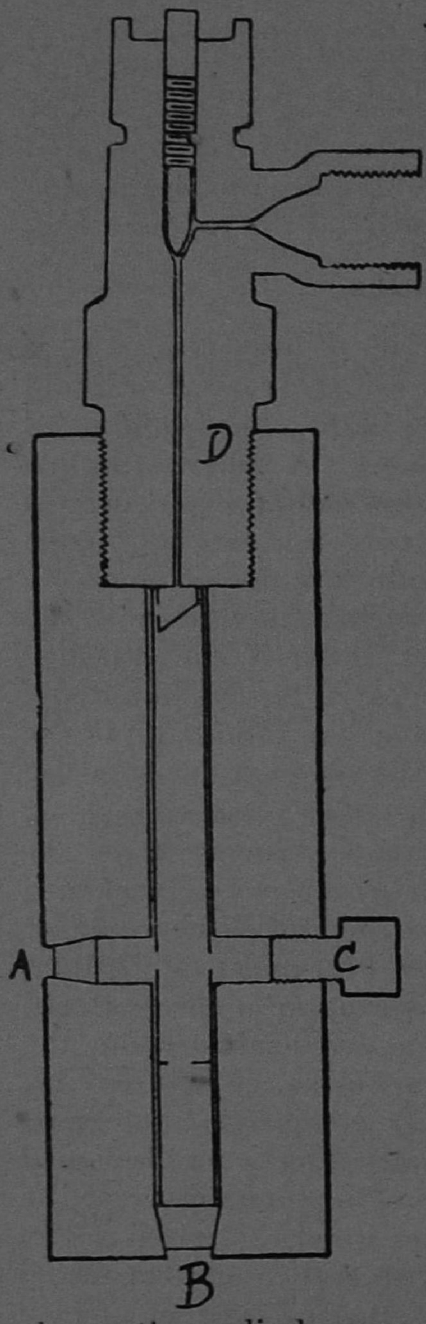
† "Molecular Diffraction of Light, Calcutta University Press, 1922, p. 61, also Phil. Mag., Jan. 1923, p. 113.

steel-tube tightly packed with cotton-wool which must have greatly impeded the inflow of the gas into the observation tube to replace that lost by leakage, and hence the density of the gas whose scattering power was measured was in all probability considerably less than that of the saturated vapour. If we assume that the pressure in the observation tube was somewhat less than that shown by the gauge and was, say 45 atmospheres, the scattering power, if it were proportional to the density would only have been about 60 times that of $CO_2$ at atmospheric pressure at the same temperature while according to the Einstein-Smoluchowski theory of scattering, it would be about 125 times. The experimental result, rightly interpreted, thus tends to support the Einstein law of scattering and not the Rayleigh law. The matter, however, appeared sufficiently important to justify a careful re-examination with apparatus so designed that no uncertainty as to the actual density of the vapour arises.

## 2. *Experimental arrangements.*

In the present investigation, two distinct series of observations were made. In the first set, the scattering medium was $CO_2$ (vapour or liquid as the case may be) enclosed in sealed glass bulbs, thus avoiding all uncertainty regarding the density of the fluid used. A spherical bulb a little over 1 cm. in diameter was blown at one end of a stout-walled capillary tube with rather a wide bore. The tube was carefully dried and exhausted, and dry $CO_2$ was introduced into it while immersed in liquid air. When the requisite quantity of carbon dioxide snow had condensed, the tube was sealed off leaving about 5 cm. attached to the bulb as a stem. Separate bulbs were prepared for the liquid and the vapour containing respectively an excess of the liquid and of the vapour. To prevent the bulbs bursting when the temperature is raised, sufficient volume for expansion is allowed in the stems attached to them. On removal from the liquid air, the carbon dioxide liquefies under the pressure. The bulb and attached stem are completely blackened over with paint except for two tiny windows one on either side of the bulb for entry and exit of a narrow but powerful pencil of sunlight and an aperture at the base of the bulb for observation of the scattered light. The stem with its bore forms a black cave against which the track of the beam through the $CO_2$ liquid or vapour as the case may be, can be conspicuously observed. The bulb is completely immersed inside a water-bath with plate-glass sides, the rear-walls being blackened so as to provide a dark field for observation. The temperature of the bath is regulated by adding lumps of ice or hot water as desired. The brightness of the track of light is compared with that in another sealed tube containing a suitable dust-free liquid like ether or benzene or in a slab of optical glass which serves as a standard and is also immersed in the bath, the same pencil of light passing through both. A rotating sector photometer with double disc placed in front of the cell enables the visual intensities of the two tracks to be equalized and their ratio thus to be determined.

Sealed bulbs, while convenient in many ways, are rather unsatisfactory optically when feeble light scattering has to be measured, owing to the unavoidable reflections from the walls of the small-sized bulbs which alone can sustain the high pressures. They are, therefore, not suitable for unsaturated vapours. It is also not possible with bulbs to work at pressures higher than the vapour tension at the given temperature. Further, owing to the convergence of the light by the spherical walls, errors are also introduced in the photometry. In order to avoid these difficulties, in the second series of experiments, a simple form of apparatus was developed by the authors (Fig. 1) which can safely withstand very high pressures and is suitable for the study of light scattering in gases and liquids.




The observation tube consisted of a massive solid steel cylinder 20 cm. long and 6·5 cm. diameter in which were drilled two cylindrical holes, one axial and the other diametral, with conical ends at A and B. Two thick glass windows were ground in at A and B, the former to admit the primary beam of light and the latter for the observation of the scattered track. After the glass windows had been ground in, a tube with apertures for the entry of the primary beam and observation of the scattered light was put in place within the steel cylinder. This tube and the steel cylinder were enamelled black, and a pin-valve was fitted to the end D and the opening at C was closed up. To secure a good black background, a plate of black glass was fitted at an angle of 45° inside the cylinder as shown. The observation tube could be connected to a pressure gauge and to the supply cylinder containing $CO_2$. Stopcocks placed on either side of the pressure gauge served to cut off its connection either with the observation tube or the supply cylinder as desired. That the readings of pressure given by the gauge were reliable was tested in the following manner. The observation cylinder was *partly* filled with liquid and kept in communication with the gauge, the connection with the supply cylinder being cut off. The readings of the gauge were taken corresponding to different temperatures of the observation cylinder and were found to agree with the saturation pressures at those temperatures given by Amagat. The supply cylinder (which had been tested to stand 200 atmospheres) was

placed in a vessel containing water and by adjustment of the temperature of the water, pressures up to 100 atmospheres could be reached. The observation tube was placed in a rectangular glass vessel containing water and its temperature could be kept constant at any desired value between 5° C and 50° C. The observation cylinder and connecting tubes were evacuated before admission of carbon dioxide. The evacuation and readmission of $CO_2$ were repeated until the track appeared a good blue with no evidence of dust particles.

For measurements of the scattering in saturated vapour, a shallow layer of liquid was allowed to condense at the bottom of the observation cylinder and the pin-valve at D closed. After a sufficient time had elapsed for the attainment of equilibrium, the intensity of the scattered light was compared with that in a standard substance as usual. For observations in the liquid in equilibrium with the vapour, the liquid was allowed to fill up more than three-fourths of the observation cylinder. The measurements of the scattering power in these two cases gave results in conformity with those obtained with the sealed bulbs.

### 3. *Experimental results: Intensity of scattering.*

(*a*) *Unsaturated vapour.*—For experiments on unsaturated vapour, the steel observation tube was cut off from the supply cylinder, and by blowing off gas through an auxiliary outlet, any desired pressure below that of saturation could be got. The following table gives the intensity of scattering at different pressures at 30° C in terms of the scattering of $CO_2$ at 0° C and 76 cm. pressure :—

TABLE I.

| Pressure in atmospheres. | Density / Density at N.T.P. | Reciprocal of compressibility in atmospheres. | Density scattering (Einstein formula). | Density scattering corrected for anisotropy. | Observed scattering. |
|---|---|---|---|---|---|
| 15 | 14·5 | 13·5 | 17·2 | 21·3 | 22 |
| 20 | 20 | 18·7 | 23·4 | 29 | 33 |
| 30 | 32·1 | 23 | 49 | 59 | 54 |
| 40 | 47 | 29·4 | 65·2 | 77 | 83 |
| 50 | 64·5 | 31·5 | 123 | 144 | 140 |
| 55 | 75·7 | 30·2 | 180 | 207 | 197 |
| 60 | 89·7 | 27·9 | 276 | 315 | 307 |
| 65 | 109 | 22·9 | 514 | 576 | 665 |
| 68 | 127 | 19·1 | 847 | 940 | 1,078 |

It will be noted from columns 2 and 6 that the observed scattering is much larger than in proportion to the density. The values in column 4 are calculated according to Einstein-Smoluchowski formula.

When the molecules are anisotropic, there is an extra scattering, the "orientation scattering" whose magnitude depends on the properties of the molecule and on the state of aggregation of the fluid. Its value has been worked out in a recent paper[1] and the total intensity at a distance $d$ of the light transversely scattered by a unit volume of the fluid in any condition is given by

$$\frac{I_0}{d^2}\left[\frac{\pi^2}{18}\frac{RT\beta}{N\lambda^4}(\mu^2-1)^2(\mu^2+2)^2+\frac{\pi^2}{2n_0\lambda^4}(\mu^2-1)^2\frac{r_1(9+4\gamma)}{6-7r_1}\right]$$

where $n$ is the number of molecules per unit volume in the fluid, $r_1$ is the ratio of the weak component to the strong in the light transversely scattered by the substance in the state of vapour at very low pressures and $\gamma$ denotes $\frac{RT\beta}{N}n_0\left(\frac{\mu^2+2}{3}\right)^2$. The other symbols have their usual meanings. The total scattering given by this formula is given in column 5 for comparison with the observed intensity of scattering given in column 6. The agreement is good except in the vicinity of the critical temperature where uncertainties in temperature and impurities in the substance have a very great effect.

TABLE II.

*(b) Saturated Vapour.*

| Temperature. | Density / Density at N.T.P. | Reciprocal of compressibility in atmospheres. | Density scattering (Einstein formula). | Density scattering corrected for anisotropy. | Observed scattering. | Remarks. |
|---|---|---|---|---|---|---|
| 0° | 48 | 20·6 | 92 | 106 | ... | |
| 5° | 57 | 21·5 | 120 | 140 | 102 | Bulb. |
| 10° | 68 | 21·9 | 180 | 205 | 195 | Do. |
| 15° | 80 | 21·0 | 300 | 340 | 347 | Do. |
| 20° | 96 | 19·7 | 560 | 620 | 567 | Do. |
| 24° | 112 | 16·0 | 920 | 1000 | 1010<br>1050 | Do.<br>Cylinder. |
| 25° | 121 | 15·0 | 970 | 1067 | 1190 | Bulb. |
| 26° | 126 | 13·7 | 1210 | 1330 | 1920<br>1860 | Do.<br>Cylinder. |
| 28° | 140 | 10·0 | 2010 | 2190 | 3630<br>3490 | Bulb.<br>Cylinder. |
| 30° | 169 | 5·9 (?) | 5100 | 5500 | 8000 | Bulb. |

[1] K. R. Ramanathan :—Proc. Ind. Assoc. for the Cultivation of Science, Vol. VIII, pp. 1—22, 1923.

TABLE III.

*(c) Liquid in equilibrium with vapour.*

| Temperature. | Density / Density at N.T.P. | Reciprocal of compressibility in atmospheres. | Density scattering (Einstein formula). | Density scattering corrected for anisotropy. | Observed scattering. | Remarks. |
|---|---|---|---|---|---|---|
| 5° | 448 | 700 | 380 | 494 | 360 | Bulb. |
| 10° | 432 | 530 | 480 | 600 | 463 | Do. |
| | | | | | 500 | Cylinder. |
| 15° | 411 | 372 | 618 | 760 | 630 | Bulb. |
| | | | | | 730 | Cylinder. |
| 20° | 387 | 220 | 905 | 1086 | 980 | Bulb. |
| | | | | | 1000 | Cylinder. |
| 23° | 369 | 146 | 1240 | 1450 | 1280 | Do. |
| 25° | 355 | 110 | 1540 | 1786 | 1800 | Bulb. |
| 27° | 340 | 65 | 2340 | 2620 | 2950 | Do. |
| 29° | 317 | 25 | 5080 | 5590 | 6200 | Do. |
| 30° | 302 | 15 | 7500 | 8350 | 11000 | Do. |
| 31° | 271 | 4 | 28700 | 31000 | 35000 | Do. |

The compressibilities at temperatures higher than 20° were obtained in the following way. The reciprocals of the compressibility at the saturation points at temperatures below 20° C. (taken from Jenkin's paper) were plotted against the temperature and taking the reciprocal of the compressibility at the critical point to be zero, a smooth curve was drawn through these points.

TABLE IV.

*(d) Liquid $CO_2$ at higher pressures.*

| Temperature. | Pressure in atmospheres. | Density / Density at N.T.P. | Reciprocal of compressibility in atmospheres. | Density scattering (Einstein formula). | Density scattering corrected for anisotropy. | Observed scattering. | Remarks. |
|---|---|---|---|---|---|---|---|
| 15° | 51 | 416 | 387 | 618 | 760 | 663 | |
| | 68 | 430 | 567 | 458 | 575 | 522 | |
| | 76 | 436 | 674 | 374 | 482 | 470 | |
| | 82 | 440 | 773 | 354 | 464 | 428 | |
| 25° | Saturation. | 355 | 110 | 1540 | 1786 | 2100 | |
| | 68 | 373 | 195 | 976 | 1122 | 1650 | |
| | 74 | 383 | 243 | 827 | 968 | 1200 | |
| | 83 | 397 | 309 | 678 | 834 | 778 | |
| | 92 | 407 | 486 | 483 | 599 | 600 | |
| 30°5 | Saturation. | 289 | 10 | 10400 | 11300 | 22500 | |
| | 72·5 | 314 | 35 | 3600 | 3900 | 5480 | The calculated values refer to 30°C. |
| | 76·5 | 343 | 83 | 1880 | 2106 | 2610 | |
| | 84·0 | 366 | 155 | 1185 | 1351 | 1097 | |
| | 86·5 | 372 | 179 | 1063 | 1220 | 940 | |

(e) *Scattering above the critical temperature.*

TABLE V.—(i) Scattering at 35° at different pressures.

| Pressure in atmospheres. | Density. / Density at N.T.P. | Reciprocal of compressibility in atmospheres. | Density scattering (Einstein formula). | Density scattering corrected for anisotropy. | Observed scattering. |
|---|---|---|---|---|---|
| 61 | 85 | 33·5 | 220 | 253 | 290 |
| 67 | 104 | 27·6 | 401 | 453 | 680 |
| 72 | 125 | 21·2 | 780 | 866 | 1170 |
| 77·5 | 177 | 13·3 | 2580 | 2830 | 3200 |
| 81 | 275 | 13·8 | 5170 | 5220 | 4230 |
| 87 | 330 | 72·1 | 2010 | 2250 | 1750 |
| 91 | ... | ... | ... | ... | 1430 |

TABLE VI.—(ii) Scattering at constant density (0·320 gm./cc.) at different temperatures above the critical temperature.

| Temperature. | Density. / Density at N.T.P. | Reciprocal of compressibility in atmospheres. | Density scattering (Einstein formula). | Density scattering corrected for anisotropy. | Observed scattering. |
|---|---|---|---|---|---|
| 32° | 165 | 8·4 | 3420 | 3730 | 4550 |
| 35° | 165 | 14·1 | 2060 | 2266 | 2730 |
| 40° | 165 | 19 | 1550 | 1705 | 1620 |
| 50° | 165 | 22 | 1380 | 1520 | 1410 |

## 4. *Polarization of the Scattered Light : Theory and Experimental Results.*

In previous papers,[1] the authors have discussed the influence of the physical condition of the substance on the imperfection of polarization of the transversely scattered light. An exact investigation of the problem has been worked out[2] on the assumption of anisotropic molecules with three principal axes. It leads to the formula

$$\gamma = \frac{2f}{f + \gamma g}$$

[1] C. V. Raman and K. Seshagiri Rao.—'Phil. Mag.,' Vol. 45, p. 625. K. R. Ramanathan :—Loc. cit.

[2] K. R. Ramanathan :—Loc. cit.

where $r$ is the ratio of the weak component to the strong in the transversely scattered light, and $\gamma$ has the meaning already indicated in the previous section. When the substance is in the gaseous state at low pressure and Boyle's law holds good, $\gamma=1$ and $r$ assumes the value $2f/(f+g)$ which has been already been denoted by $r_1$

Also

$$g-\frac{4}{3}f=\frac{9}{16\pi^2 n_0^2}\left(\frac{\mu^2-1}{\mu^2+2}\right)^2$$

The formula indicates that when the scattering is very large, e.g., in the neighbourhood of the critical point, it is almost completely polarized, while in other cases, e.g., when the substance is in the liquid state much below the critical temperature, the polarization is markedly less perfect than in the scattering by the vapour at low pressures. While these indications of theory are in qualitative agreement with facts, it is found that in the case of many liquids, there are considerable differences between theory and observation in the quantitative data, indicating that the assumption of a random orientation of the molecules made in the theory is not generally valid. This makes it all the more important that as many different substances as possible should be examined.

The problem of determining accurately the state of polarization of light scattered by a fluid under high pressures is not without serious experimental difficulties. The principal source of error is the unavoidable strain and consequent ælotropy of the glass walls or the glass window through which the scattered light is observed. If the strain were perfectly symmetrical about the direction of observation, no error would arise, but this condition is not easy to secure, especially when a conical glass window has to be pressed home into a metal recess provided for it to make it perfectly leak-tight. Small sealed bulbs are also not quite suitable in this type of work owing to the very imperfect background which they furnish for observing the fainter component of polarization. In view, however, of the fact that even an approximate determination of the state of polarization under different conditions would be of interest, attempts were made to measure the effect with the apparatus used by the authors. The vapour or liquid inside the chamber was illuminated by a narrow horizontal beam of sunlight and on examination with a double-image prism set so as to transmit vertical and horizontal vibration, it was found that even near the critical point, both images were bright, but that across the weaker one, there was an intense black band running obliquely. The glass window was obviously under strain, but by isolating the portion of the glass wall transmitting the central portion of the black band alone by means of a narrow slit ( nearly 1 mm. wide) placed in contact with the window, measurements of polarization were made as usual with a double-image prism and nicol.

The following tables contain a summary of the results :—

### 5. *Imperfection of Polarization.*

TABLE VII.

(i) *Unsaturated vapour at 30° C.*

| Pressure in atmospheres. | Ratio : Weak component. / Strong component. | |
|---|---|---|
| | Observed. | Calculated. |
| 30 | 9 % | 8 % |
| 40 | 8 | 6 |
| 50 | 6 | 4·9 |
| 60 | 4·5 | 3·1 |
| 65 | 4 | 2 |

(ii) *Saturated vapour.*

| Temperature. | Ratio : Weak component. / Strong component. | |
|---|---|---|
| | Observed. | Calculated. |
| 15° | 5·8 | 2·6 |
| 20° | 4 | 2·1 |
| 25° | 3 | 1·2 |
| 30° | 1·5 | 0·3 |

(iii) *Liquid in equilibrium with vapour.*

| Temperature. | Ratio : Weak component. / Strong component. | |
|---|---|---|
| | Observed. | Calculated. |
| 10° | 14 | 10·5 |
| 15° | 10 | 7 |
| 20° | 8 | 6 |
| 25° | 5 | 3·8 |
| 28° | 3 | 1·4 |

(iv) *Liquid under higher pressures.*

| Temperature. | Pressure in atmospheres. | Ratio : $\frac{\text{Weak component.}}{\text{Strong component.}}$ | |
|---|---|---|---|
| | | Observed. | Calculated. |
| 20° | 92<br>80 | 13<br>10 | 14<br>9 |
| 25° | 90 | 9 | 8 |

The observed values are uniformly a little too high. This is probably due to the fact that the slit used has a finite width and transmits light to a small distance on either side of the centre of the black band. The actual course of values, however, follows the indications of theory.

## *Summary and Conclusion.*

The paper describes a simple form of apparatus which enables the intensity and state of polarization of the light scattered by gases and liquids at high pressures to be measured. Results obtained with carbon dioxide are given, the noteworthy features being the following :—

(1) the scattering in carbon dioxide in the condition of unsaturated vapour below the critical temperature is not proportional to the density, but increases much more rapidly as the saturation pressure is approached, and the polarization of the transversely scattered light becomes sensibly more and more *perfect*.

(2) The scattering in the saturated vapour and in the liquid phase in equilibrium with it has also been studied. When the liquid is further compressed by application of pressure in excess of the vapour tension, its light-scattering power shows a striking diminution, and the polarization becomes markedly more *imperfect*.

(3) Above the critical temperature, the scattering power at first increases with rise of pressure, reaches a maximum and diminishes again.

(4) Except very close to the critical temperature, the experimental results agree well with the Einstein-Smoluchowski theory of scattering when the effect of molecular ælotropy is taken into account.

We have, in conclusion, to express our cordial thanks to Messrs. The Lightfoot Refrigeration Company of Calcutta, who gave us much assistance in fitting up the high-pressure apparatus and in other ways.

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# ON THE MOLECULAR SCATTERING OF LIGHT IN DENSE VAPOURS AND GASES

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## 1. *Introduction.*

As is well known, the theory advanced by the late Lord Rayleigh* explaining the blue light of the sky as due to the molecular scattering of sunlight has of recent years been amply confirmed by accurate measurements of sky-radiation and of the attenuation of the sun's rays in traversing the earth's atmosphere, and also by the laboratory experiments of Cabannes † and of the present Lord Rayleigh ‡ which have demonstrated the scattering of light by dust-free gases and shown that its magnitude is in agreement with the theory. Apart from its special application to the explanation of the blue light of the sky, the subject of the molecular scattering of light possesses very great interest, standing as it does in intimate relationship with the fundamental problems of optics, such as the propagation of light and the reflexion, refraction, dispersion, and extinction of light in transparent media. Its study has already yielded information which is of first-rate importance in testing theories of atomic and molecular structure, and promises to prove even more fruitful in future in the same direction. It is also not improbable that the study of the problems of molecular scattering of light may serve to elucidate the nature of radiation itself, that is, to determine whether it consists of some form of continuous disturbance moving through space, as contemplated by Maxwell's electro-magnetic theory, or whether it consists of discrete entities or "quanta," as conceived of by Einstein. It is proposed in this paper to consider the very important problem of the scattering of light in *dense* media, such as vapours and gases under high pressure, in which circumstances, as was pointed out by the late Lord Rayleigh himself, the simple treatment proposed by him is not applicable. Fresh experimental evidence bearing on the subject will also be referred to.

* Phil. Mag. xlvii, pp. 375--384 (1899). Scientific Papers, vol. iv, p. 397.
† *Annales de Physique*, xv. pp. 1--150.
Proc. Roy. Soc., xciv, p. 453 (1918) *et seq.*

## 2. *Rayleigh's Theory of Light-scattering.*

As a preliminary to the discussion of the problem of light-scattering in highly compressed gases and vapours, it is useful to recall very briefly the principles on which the case of gases under ordinary conditions was dealt with by Lord Rayleigh. Reduced to its essentials, the treatment is on the following lines :—

The individual molecules in a gas through which the primary waves of light pass are regarded as secondary sources of radiation, each molecule acting more or less as it would in the absence of its neighbours. There is, of course, a definite phase-relation between the primary wave when it reaches a given molecule and the secondary wave emitted from it. *In the direction of propagation of the primary waves* the secondary radiations emitted by all the molecules in a given layer are in identical phase, for the differences in the phase of the primary wave when it reaches different molecules are exactly compensated by the acceleration or retardation due to the scattered waves having to traverse a shorter or greater path, as the case may be. *In other directions*, however, owing to the molecules being distributed at random within the volume of the gas, the phases of the scattered waves do not stand in any invariable relation to each other, and hence, in order to find the average expectation of intensity of the scattered light emerging from within the gas, the *intensities*, not the amplitudes of the waves scattered by the individual molecules, should be added up. In all ordinary cases there is very little difference of phase between the primary wave reaching an individual molecule and the secondary wave sent out by it, so far as the direction of original propagation of the wave is concerned. When, however, the effect of all the molecules contained in a stratum parallel to the plane of the primary wave is integrated by the usual method of subdivision of the stratum into Fresnel zones, and the resultant is combined with the primary wave, a change of phase appears which may be identified as the retardation associated with the passage of waves through a refractive medium. A relation is thus obtained between the scattering power of the molecules, their number per unit volume, and the refractivity of the medium. Thus, taking the light-vector in the primary waves to be represented by $R_0 \cos(\omega t - lx)$, where $x$ is measured from the position of the scattering molecule, the vector in the scattered wave arising from it may be written as

$$A_1 \cos(\omega t - lr)\, R_0 \sin\theta / r, \qquad (1)$$

when $r$ is the distance from the molecule and $\theta$ is the angle between the vibration at the origin and the scattered ray. On carrying out the calculations indicated, the relation obtained is

$$n_1 A_1^2 = \frac{4\pi^2(\mu-1)^2}{n_1 \lambda^4} \qquad (2)$$

when $n_1$ is the number of molecules in unit volume, $\lambda$ is the wave-length of the light, and $\mu$ is the refractive index of the gas.

The energy scattered by the molecules in the interior of the gas must be derived from the primary beam, and hence the intensity of the latter must suffer an attenuation as it passes through the medium. The coefficient of attenuation may be readily evaluated by a simple calculation of the total energy scattered by an individual molecule, and then multiplying this by the number $n_1$ of molecules per unit volume. We thus obtain the intensity of the transmitted light to be $I = I_0 e^{-kx}$, where $k$ the coefficient of attenuation is given by the relation

$$k = \frac{32\pi^3(\mu-1)^2}{3n_1\lambda^4} \qquad (3)$$

This expression for the attenuation coefficient may also be derived directly by a more accurate investigation, which does not neglect the small difference of phase between the primary wave and the secondary waves originating at a molecule. It is then found that on compounding the effects of the primary wave with those of the secondary wave arising from a stratum of molecules, there appears, in addition to the alteration of phase of the primary wave, also a small diminution in its intensity which is exactly that expected in view of the lateral scattering of part of the energy.

### 3. *Justification of the Principle of Random Phase.*

It will be seen from the foregoing that the Rayleigh law of scattering depends for its validity on the principle that the phases of the waves laterally scattered by the individual molecules are absolutely at random. This point is clearly brought out in the detailed analyses of the problem which have been given by H. A. Lorentz * and by the late Lord Rayleigh himself†, and it appears that the necessary random character of the phases of the scattered waves can only arise from a random arrangement in space of the molecules under consideration. If we deny the random character of this distribution of phase of the scattered waves, we must also deny the applicability of Rayleigh's law expressing the intensity of the scattered light in terms of the refractivity of the medium. The fact that even in a gas at atmospheric pressure there are about $10^6$ molecules in a cube of the size of a wave-lengh of light, so that the scattered waves arising from adjacent molecules differ in phase by only $10^{-2}$ of the period, has been felt as a difficulty by some writers in this connexion. In fact, Larmor‡ has raised the question whether, in view of this closeness of packing, we are really justified in considering the phases of the individual scattered waves to be distributed entirely at random. It may be easily shown, however, that no appreciable deviation from a random distribution of phase, and

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* Proc. Roy. Soc. of Sciences, Amsterdam, xiii, p. 92 (1910).
† Phil. Mag., xxxvi, pp. 429—449 (1918 .
‡ Phil. Mag., xxxvii, p. 161 (1919).

therefore, also, from the Rayleigh law of scattering, can arise so long as the pressure volume relation of the gas does not sensibly deviate from Boyle's law. For, all that is necessary is that the chance that a given molecule finds itself in a specified finite element of volume should be a random one, that is, is sensibly uninfluenced by the other molecules in the gas. This is true provided the total volume occupied by all the molecules, or rather by all their spheres of mutual action, forms a small fraction of the total space in the containing vessel, which is obviously also the condition that the compressibility of the gas should not appreciably deviate from that given by Boyle's law.

Larmor has made the suggestion* that Rayleigh's principle of random phase is not correct in the form in which it is stated, but that the random character of the phases of the scattered waves when they reach the observer is secured by the Doppler effect, due to the motion of the scattering molecules. The view he proposes is, in fact, that the phases of the scattered radiations emerging from the column of gas may be correlated at first, but after traversing $10^6$ wave-lengths, or 50 cms., they would have become fortuitous and the energy-effects thus additive. Larmor's suggestion is, however, not acceptable. For, if it were correct, we should find that the aggregate intensity of the scattered light should be small immediately after emergence from the column of gas, that is, when it is observed within a distance of a centimetre or two from the track of the primary beam, and should increase at a greater distance from it. Such a result is obviously quite inadmissible, besides being contrary to experience. The fallacy lies in Larmor's assumption that the change of wave-length (Doppler effect) has an effect on the relative phases of the scattered waves, whereas in reality it has none. To make this clear, we may consider two neighbouring molecules A and B. The scattered waves originating from them travel outwards with an identical velocity which is quite unaffected by any movements of these molecules. The phase-difference at any epoch therefore remains unaffected as the waves move out, being exactly the same as when the portions of the wave-train under consideration left the molecules. In other words, the phase-difference at each stage is exactly the same as if the molecules had remained fixed from the instant of emission of the scattered light. The scattering from any appreciable volume of gas would thus remain unaffected if all the molecules were assumed suddenly to be fixed in their instantaneous positions, and the Doppler effect due to their movement exerts no influence whatever on the observed results. Larmor's suggestion, therefore, clearly fails, and we have to fall back upon the view already expressed that the *principle of random phase of the scattered waves rests upon the random character of the distribution of the molecules in space in a gas obeying Boyle's law.*

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* *Loc. cit*

## 4. *Application of Boltzmann's Distribution Law.*

It is clear from the preceding discussion that if the distribution of the molecules of a gas or vapour in space is *not* a random arrangement, the intensity of the light scattered would not be given by the Rayleigh law, that is, would cease to be simply proportional to the number of molecules per unit volume. In the usual treatments of the kinetic theory of gases, the molecules are conceived to exert forces on each other, and if the time during which the forces acting on any individual molecule are sensible forms an appreciable fraction of the whole time, the arrangement of the molecules would not be a random one. The influence of the molecules on each other would not then be negligible, and the energy-effects of the individual molecules could not be added up to find the total light scattered in the manner contemplated by the simple theory. It is, however, possible to make a calculation of the altered scattering power of the gas. Let $\phi(r)$ be the law of repulsive force between any two molecules whose centres are at a distance $r$ from each other. By a suitable assumption regarding the nature of $\phi(r)$, it is possible to include in this function the cohesive or van der Waals's forces which act when the molecules are not in collision with each other, and also the large repulsive forces occurring during actual impact. According to a well-known theorem due to Boltzmann*, the chance that two molecules find themselves at a finite distance $r$ apart is less than the chance that they are at a very great distance apart in the ratio.

$$e^{-\frac{1}{RT}\int_r^\infty \phi(r)dr}, \qquad (4)$$

where $\int_r^\infty \phi(r)\,dr$ obviously expresses the potential energy of the configuration. The probability of groups of three, four, or more molecules being found at specified distances apart may be similarly expressed in terms of the potential energies of the respective configurations. If we assume that the deviation from Boyle's law is not very large, expression (4) will suffice to enable us to take into account the mutual influence of the molecules in determining their ordering in space. Consider a sphere of radius $l$ drawn round the instantaneous position of a given molecule as centre. If $n$ be the whole (actual) number of molecules in the volume of the gas or vapour, the number to be expected within this sphere of volume $\frac{4}{3}\pi l^3$ is

$$\int_0^l A.\, 4\pi r^2 dr\, e^{-\frac{1}{RT}\int_r^\infty \phi(r)dr} \qquad (5)$$

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* *Vorlesungen über Gastheorie*, II. See also Jeans' "Dynamical Theory of Gases, rd ed., p. 132.

where A is a constant to be presently determined. Integrating by parts, (5) reduces to

$$A\left[\frac{4}{3}\pi r^3 e^{-\frac{1}{RT}\int_r^\infty \phi(r)\,dr} - \frac{1}{RT}\int_0 \frac{4}{3}\pi r^3 \phi(r)\,dr\, e^{-\frac{1}{RT}\int_r^\infty \phi(r)dr}\right]_0^l . \quad (6)$$

To enable this expression to be reduced, we will assume that the force $\phi(r)$ between two molecules vanishes sensibly when $r \geqq \sigma$, where $\sigma$ is the range of molecular action. The expression (6) then reduces to

$$A.\frac{4}{3}\pi l^3 - \frac{A}{3RT}\int_0^\sigma 4\pi r^2 \phi(r)\,dr\, e^{-\frac{1}{RT}\int_r^\infty \phi(r)dr}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

provided $l \geqq \sigma$. When $l$ is very great, the first term in (7) will be very large in comparison with the second, and since (7) must then give the total number of molecules, we find at once $A = \frac{n}{v}$. We may denote the integral in (7) by C; and putting $l = \sigma$, we find that, on the average, the number of molecules which we may expect to find within the sphere of action of the specified molecule is

$$\frac{n}{v} . \tfrac{4}{3}\pi\sigma^3 - \frac{nC}{v.3RT}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and is thus smaller than the number corresponding to a random distribution of the molecules by $\frac{nC}{v\,.\,3RT}$. (If C be negative, the number will be greater.)

In order to evaluate the intensity of the scattered light, we may now apply the general method developed by the late Lord Rayleigh*. The disturbance due to the scattered waves may be represented by the summation

$$\Sigma \cos(pt + \epsilon_1), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $\epsilon_1$ represents the phase of the scattered wave arising from a molecule and is easily expressed in terms of the position of the molecule and the directions of the incident and scattered rays. The *intensity* of the scattered light is obviously represented by

$$\begin{aligned} &[\cos\epsilon_1 + \cos\epsilon_2 + \cos\epsilon_3 + \ldots]^2 \\ &+ [\sin\epsilon_1 + \sin\epsilon_2 + \sin\epsilon_3 + \ldots]^2 \\ &= n + 2\,\Sigma\cos(\epsilon_1 - \epsilon_2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10) \end{aligned}$$

where $n$ is the number of molecules and the summation $\Sigma\cos(\epsilon_1 - \epsilon_1)$ has to be made for all the $\frac{1}{2}n(n-1)$ pairs of molecules contained in the volume. For a random distribution, $\Sigma\cos(\epsilon_1 - \epsilon_2)$ vanishes, as has

* Phil. Mag. xxxvi, pp. 429-449 (1918).

been shown by Lorentz and by Rayleigh. In the present case, the distribution differs from a random one in that the average number of molecules present within the sphere of action of a molecule is smaller by $\frac{n}{v}\frac{C}{3RT}$. The summation indicated in (10) will not therefore reduce to $n$ simply. Since the radius of action $\sigma$ of the molecules is much less than the wave-length of the light, the value of $(\epsilon_1 - \epsilon_2)$ for the missing molecules may without appreciable error be taken to be zero, and hence, when the summation is carried out for all the molecules in the volume $v$, (10) will reduce to

$$n\left(1 - \frac{n}{v}\cdot\frac{C}{3RT}\right). \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From this it is seen that if C be positive, the intensity of the scattered light is less than that given by the Rayleigh law, while if C be negative, it is *greater*.

In order to interpret the result contained in (11), we notice that the integral in the second term of (7) which we have denoted by C when multiplied by $\frac{1}{2}\frac{n^2}{v^2}$ represents the *virial function* for the gas or vapour. The virial equation is in fact simply*

$$pv = nRT + \frac{1}{6}\frac{n^2}{v}C. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

By differentiating (12), the compressibility $\beta$ of the gas or vapour may be written as

$$\beta = -\frac{1}{v}\frac{dv}{dp} = \frac{1}{n\frac{RT}{v}\left(1 + \frac{n}{v}\frac{C}{3RT}\right)} \quad . \quad . \quad . \quad (13)$$

$$= \frac{v}{nRT}\left(1 - \frac{n}{v}\frac{C}{3RT}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

to the same decree of approximation as used previously. On comparing (14) with (11), it is seen that the intensity of the light scattered per unit of volume, instead of being proportional to $\frac{n}{v}$ as required by the Rayleigh law, is proportional to

$$\frac{n^2}{v^2}RT\beta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and thus varies directly as the absolute temperature, the square of the density of the substance and its compressibility. In the case of a gas

* This agrees with Keesom's approximate equation of state, containing only the first two terms in the expansion of the virial function. Proc. Roy. Acad. Sciences, Amsterdam, vol. xv, p. 264.

obeying Boyle's law, $\beta = \frac{1}{p}$ and $pv = n\mathrm{RT}$, and (15) becomes simply $\frac{n}{v}$ in agreement with the Rayleigh law.

### 5. *The Theory of Density Fluctuations.*

The result deduced by us in the preceding section from the principles of the kinetic theory for the case of moderately compressed gases agrees with the general formula obtained in an entirely different manner by Einstein* in developing an explanation given by Smoluchowski † of the phenomenon of opalescence exhibited by fluids in the vicinity of the critical state. Einstein's reasoning is of a very general character and makes no use whatever of the molecular hypothesis. It is based on the following train of ideas. If, in the condition of equilibrium, the medium is conceived of as a completely uniform homogeneous system, there can be no scattering of the light-waves passing through it. Actually, however, as Smoluchowski showed from thermodynamical considerations, the density of the substance must vary from point to point, and also fluctuate from instant to instant, the density as measured by our ordinary appliances being merely a statistical average. Hence, in framing the electromagnetic equations, the dielectric constant (which is assumed to vary with the density in the manner contemplated by the Lorentz-Mossotti formula) must be regarded as varying from point to point, and the solution of the equations for wave-propagation contains, besides the regularly transmitted waves, also an opalescence radiation which is a volume-effect and represents the scattered light resulting from the local inequalities of density. Einstein's treatment naturally therefore falls into two parts: firstly, the determination of the magnitude of the fluctuations of the dielectric constant for the elements of volume; secondly, the calculation of the opalescent radiation.

The magnitude of the density-fluctuations is calculated by Einstein in the following manner :—Boltzmann's well-known thermodynamical principle connects the entropy S of a system with the probability W to which the entropy S relates by the equation.

$$\mathrm{S} = \mathrm{R} \log \mathrm{W} + \text{constant}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where R is the gas-constant. Einstein points out that the entropy S of the whole system does not completely define the physical conditions of the small individual parts of the system at any instant, and hence (16) should be understood as referring to an *ensemble* of different possible conditions of the system in each of which its entropy is S. If we consider particular parts of the system and particular instants of time, fluctuations from the ideal thermodynamic equilibrium must appear

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* *Annalen der Physik*, xxxiii, p. 1294 (1910).
† *Loc. cit.* xxv, p. 205 (1908).

the magnitude of which is determined by the corresponding changes of entropy of the parts of the system. For an isothermal compression or rarefaction, the change of entropy is simply the work done divided by the absolute temperature. Boltzmann's theorem may be written in the form.

$$W = e^{\frac{S-S_0}{R}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where $S_0$ is the entropy in the state of thermodynamic equilibrium. Taking $\nu$ to be the deviation of some observable physical variable, *e.g.* in this case the density, from the value corresponding to thermodynamic equilibrium, Einstein writes (17) in the form.

$$W(\nu)d\nu = Ae^{-\frac{1}{2RT}\alpha\nu^2} d\nu, \quad . \quad . \quad . \quad . \quad (18)$$

where $W(\nu)d\nu$ is the probability that $\nu$ lies between $\nu$ and $\nu+d\nu$, A is a constant, and $\frac{1}{2}\alpha\nu^2$ is the work done in altering $\nu$ from 0 to $\nu$. (18) evidently has the same form as Gauss's error-law, and it follows that

$$\overline{\tfrac{1}{2}\alpha\nu^2} = \tfrac{1}{2}RT. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where the bar indicates the *mean* value of the quantity under consideration. If we identify $\nu$ with $(\Delta\rho)$ the fluctuation of density, its mean square may be evaluated from (19) and written in the form

$$\overline{(\Delta\rho)^2} = \frac{RT\beta\rho_0^2}{\phi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where $\beta$ is the isothermal compressibility, $\phi$ is the small element of volume under consideration, and $\rho_0$ is the mean density.

For the deduction of the light-scattering from (21) with the aid of Maxwell's electromagnetic equations, reference should be made to Einstein's original paper. We may follow here an abbreviated treatment which gives an identical result.

At right angles to the incident light the intensity of scattered light is given by the expression.*

$$\frac{\pi^2\phi^2(\Delta\epsilon)^2\,1}{2\lambda^4r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$(\Delta\epsilon)$ being the variation of the dielectric constant.

Now, as the individual local variations of the dielectric constant are irregularly distributed, the phases of the various scattered beams are also quite arbitrary, and hence for calculating the total intensity of

* Rayleigh, Phil. Mag., p. 81 (1881); Sc. Papers, vol. i., p. 526.

scattered light we have merely to sum up the above expression over the total volume $v$. The expression contains a factor.

$$\Sigma(\Delta\epsilon)^2\phi^2,$$

which may be evaluated by use of the Mosotti-Lorentz law

$$\frac{\epsilon-1}{\epsilon+2}=\text{const. }\rho.$$

Differentiating, we obtain

$$(\Delta\epsilon)^2=\frac{(\epsilon-1)^2(\epsilon+2)^2}{9}\left(\frac{\Delta\rho}{\rho_0}\right)^2 \quad . \quad . \quad . \quad . \quad . \quad (22$$

Substituting in this the value given above for fluctuation of density we obtain

$$\frac{(\epsilon-1)^2(\epsilon+2)^2}{9}=\text{RT}\beta\Sigma\phi=\text{RT}\beta\frac{(\epsilon-1)^2(\epsilon+2)^2}{9}.v. \quad . \quad (23$$

Thus the intensity of light scattered by a cubic centimetre of fluid at right angles to the incident rays is

$$\frac{\pi^2}{18}\text{RT}\beta\frac{(\epsilon-1)^2(\epsilon+2)^2}{\lambda^4}=\frac{\pi^2}{18}\text{RT}\beta\frac{(\mu^2-1)^2(\mu^2+2)^2}{\lambda^4}. \quad . \quad (24)$$

In the cases of gases and vapours, whether obeying Boyle's law or not, the formula (24) may be appreciably simplified by assuming $(\mu^2+2)=3$, and $(\mu^2-1)^2=4(\mu-1)^2$ approximately, and it may then be written in the form

$$\frac{2\pi^2(\mu-1)^2\text{RT}\beta}{\lambda^4}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

If the gas or vapour obeys Boyle's law, $\beta=\frac{1}{p}$ and $pv=n\text{RT}$, and (25) becomes identical with the Rayleigh law. In other cases, (25) is seen to agree with formula (15) when the omitted multiplying factors are restored.

It may be pointed out that the expression giving the magnitude of the density-fluctuation might have been derived immediately from the principle of equipartition of energy, as is indeed evident from the form of the relation (19). In the case of a gas obeying Boyle's law in which the molecules are distributed at random throughout the space, the mean square of the density-fluctuation may also be derived by direct application of the theory of probabilities, and the intensity of the scattering calculated therefrom. This has been done by Lorentz*, and the result naturally agrees with that obtained by Rayleigh.

* Proc. Roy. Soc. Amsterdam xii, p. 92 (1911).

### 6. *Experimental Tests of the Einstein-Smoluchowski Formula.*

The expression given by Einstein for the light-scattering in a direction transverse to the primary beam, viz. :

$$\frac{\pi^2}{18}\frac{R_1 T\beta}{N_1}\frac{(\mu^2-1)^2(\mu^2+2)^2}{\lambda_4},$$

where $R_1$ and $N_1$ represent the gas-constant and the Avogadro-number respectively for a *gram-molecule*, was originally developed by him to explain the opalescence exhibited by fluids in the vicinity of the critical state. It should, however, possess a far wider and *general* application, and indeed be regarded as superseding the Rayleigh law of scattering, which should only be valid in the special case of gases accurately obeying Boyle's law. It is thus of great importance to test the validity of the Einstein-Smoluchowski formula over a very wide range of cases. So far as the authors are aware, the only experimental tests that have so far been made of it for the case of a single substance in the gaseous state are those of Kammerlingh Onnes and Keesom* on the opalescence of ethylene vapour, but the work of these investigators was confined to a range of only 2·5 degrees of temperature *above* the critical temperature of this substance. A far more comprehensive and general test of the formula for several substances over the widest possible range of temperatures and pressures is obviously desirable, and researches with this object have been undertaken in the authors' laboratory. The first substance chosen was ether. This substance has a high refractivity and therefore a large scattering power in the state of vapour, and its critical temperature and pressure are moderate, and it also possesses a high degree of chemical stability under the action of heat and light. It is therefore very well suited for quantitative work. The detailed account of the determinations carried out with it by one of us (K. R. Ramanathan) will be published in a separate paper, and it will suffice here to indicate the general scope of the work and the results obtained. The light-scattering power of ether has been determined separately for the substance in the saturated vapour and in the liquid phases for temperatures from 30° C. to the critical temperature 194° C., and for the gaseous phase from 194° C. to 217° C. The vapour and gaseous phases deviate very largely from Boyle's law, the compressibility being larger than the reciprocal of the pressure, especially at the higher temperatures, and the measurements throughout the whole range show that the *Rayleigh law of scattering completely breaks down* and strikingly confirm the correctness of the Einstein-Smoluchowski formula. The scattering power of the vapour when it is dense is in fact several times larger than that given by the Rayleigh law, and this feature is more and more pronounced as the critical temperature is approached from either

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* *Loc. cit.* (1908).

side. The Einstein-Smoluchowski formula also shows itself to be equally applicable to the case of liquids over the whole range of temperature tried.

## 7. *Polarization of the Scattered Light.*

It should be noted that, according to Einstein's investigation, the light scattered in a direction transverse to the primary beam should be completely polarized. Actually, however, this is not the case. The imperfectness of the polarization of the light scattered by gases was first discovered by Strutt (the present Lord Rayleigh), and measurements of the magnitude of the effect have been made by a photographic method by him * and by Cabannes † and also by Gans ‡. The imperfect polarization can be detected visually even in the case of dust-free air at atmospheric pressure §, and with the gases at high pressure the increased intensity enables *visual measurements* to be carried out. In the case of ether vapour, the effect is very feeble, the polarization in the transversely scattered light being nearly complete (about 98·5 per cent), but the great intensity of the scattered light enables *visual measurements* to be carried out, and it is found that with increasing density of the vapour, the percentage of polarization does not appreciably change. In the case of the liquid, specially interesting effects are observed which will be dealt with in a separate paper.

Cabannes ‖ has shown that owing to the imperfect polarization, the intensity of the transversely scattered light is increased and is greater than that given by the Rayleigh law in the ratio $\frac{6(1+\rho)}{6-7\rho}$, where $\rho$ is the ratio of the weaker to the stronger component of polarization. It is found that the Einstein-Smoluchowski formula should be modified by a similar correcting factor in order to give results in agreement with experiment. The correction becomes very important when $\rho$ is large.

## 8. *Relation of Molecular Scattering to Critical Opalescence.*

As we have already seen, the Einstein-Smoluchowski formula shows that there is a perfect continuity between the comparatively feeble light-scattering shown by gases and vapours under ordinary conditions and the extremely large scattering or opalescence which develops as the critical state is approached. At the critical point itself, the compressibility of the substance is infinite, and it follows that the Einstein-Smoluchowski formula gives an infinite value for the scattering power. This is obviously inadmissible, and Einstein ¶ himself has pointed out

* Proc. Roy. Soc., xciv, p. 453 (1918).
† *Ann de Physique*, xv, pp. 1–150.
‡ *Ann der Physik*, lxv, p. 97 (1921).
§ 'Nature,' Jan. 19, 1922.
‖ *Loc. cit.*
¶ *Ann. der Physik*, xxxiii, p. 1275 (1910).

that for a *very minute* region at and round the critical point, the neglect of second-order terms in the expression for the work done in altering the density is not permissible and the formula requires modification. This point has, however, not much importance for our present purpose, as the range of temperature over which the neglect of the second-order terms is not permissible is exceedingly small. It may be mentioned that the matter has been further discussed by Ornstein and Zernike* who have proposed an amended formula applicable in the immediate neighbourhood of the critical point which leads to a finite value for the scattering at this point. The bearing of Ornstein and Zernike's results on the phenomena observed with ether will be dealt with separately.

### 9. *The Case of Carbon Dioxide and the permanent gases.*

The experimental confirmation of the Einstein-Smoluchowski formula for the case of ether vapour, and also in the case of various ordinary liquids, shows that its theoretical basis is thoroughly firm and that the formula may be justly expected to apply equally well in the case of other gases and vapours. It is therefore very important that the case of carbon dioxide and the permanent gases, *e.g.*, oxygen, nitrogen, argon, etc., should be thoroughly investigated. The scattering power of saturated carbon dioxide vapour at 21° C. (that is, ten degrees below the critical temperature) has been determined by the present Lord Rayleigh, and found to be 102 times that of the gas at atmospheric pressure. The compressibility of carbon dioxide at this temperature is very great, and the Einstein-Smoluchowski formula shows that the scattering power of saturated carbon dioxide at 21° C. should have been about 855 times that of the gas at atmospheric pressure. The observed result thus apparently supports the Rayleigh law of scattering (the density of carbon dioxide at this temperature being about 110 times the density of atmospheric pressures), and not the Einstein-Smoluchowski formula. The experimental result is however open to question, as Rayleigh mentions that his observation tube had a leak, and the density of the gas was therefore probably much less than that corresponding to the saturation pressure. Some observations made in a Cailletet tube containing $CO_2$ liquid and vapour by the authors show that both carbon dioxide liquid and vapour scatter light very strongly at and for a few degrees below the critical temperature, but the scattering power falls off very quickly with decreasing temperature. It is hoped to carry out a series of measurements at different temperatures with improved apparatus, and to obtain data in order decisively to settle the question whether the Einstein-Smoluchowski formula does really break down for carbon dioxide. Probably standing in very close relation to this is the fact that has been observed by Kammerlingh Onnes and his co-workers at the Leiden Laboratory, that pure oxygen,

* Proc. Amsterdam, xvii, p. 793 (1914.)

nitrogen*, and argon do not show the phenomenon of critical opalescence. It is obviously of the greatest importance to investigate whether in these cases the Einstein-Smoluchowski formula is applicable or not.

Till further data are available, it is probably not safe to venture an opinion, but it seems clear that the applicability of the thermodynamic reasoning of Einstein and Smoluchowski stands on an unchallengeable basis at least at ordinary temperatures and so far as gases and liquids are concerned. It will be noticed that the formula was derived on the basis of the classical theory of light in which it is assumed to consist of some form of continuous wave-propagation. In view of recent work in various modern fields of physics, and the known failure of the classical theory in explaining the facts regarding the emission and absorption of light, the question arises whether we are justified in assuming that the classical wave theory is necessarily capable of giving a strict quantitative explanation of the facts regarding the molecular scattering of light? Is it not possible that in the case of substances whose molecules have a relatively small light-scattering power, the infinite sub-divisibility of the energy of the incident waves which the classical theory assumes might break down? Then again is it not possible that the statistical-mechanical considerations on which the validity of Boltzmann's principle rests might require modification in the sense of the quantum theory, particularly in dealing with fluids at low temperatures? The answer to these questions can only be given when a more thorough experimental investigation of the facts of molecular scattering in dense vapours has been carried out. Such investigation has been undertaken by the authors, and it is hoped that before long the necessary data will be available.

## 10. *Summary.*

The paper considers the problem of the molecular scattering of light in dense vapours and gases *not* obeying Boyle's law. The following are the principal results :—

(1) It is shown by a discussion that the Rayleigh law of scattering which is based on the assumption of a random distribution of the molecules in space, should not be applicable in these cases.

(2) Assuming the non-random distribution of the molecules in space to be given by Boltzmann's theorem, a calculation is made of the scattering power of the medium. The result obtained is interpreted with the aid of the virial equation, and it is shown that the scattering power per unit volume is proportional to the absolute temperature, to the square of the density of the substance, and to its compressibility. If the gas obeys Boyle's law, the expression reduces to the Rayleigh law.

* Proc. Amsterdam Academy, xviii, p. 950 (1915).

(3) The result thus deduced directly from the principles of the kinetic theory agrees with the general formula derived from the thermodynamical theory of density fluctuations, developed by Einstein and Smoluchowski of which a brief account is given.

(4) Experiments carried out with ether vapour and liquid over a large range of temperature both below and above the critical point completely confirm the Einstein-Smoluchowski formula for this substance.

(5) The corrections of the formula necessary in view of the imperfectness of the polarization of the transversely scattered light, and also in the immediate neighbourhood of the critical point when the compressibility becomes excessively great, are indicated.

(6) The cases of carbon dioxide and of the permanent gases are referred to and the possible significance of the results obtained in their cases is discussed.

Calcutta, India,
April 22nd, 1922.

*Note added in proof* (*6th August*): Since the paper was sent in, experiments on the light-scattering in the vapours of benzene and pentane at different temperatures and also in *carbon dioxide* at high pressure contained in sealed bulbs have been carried out, and these definitely confirm the Einstein-Smoluchowski formula and show that the Rayleigh law of scattering is not valid except in gases obeying Boyle's law.

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# THE MOLECULAR SCATTERING OF LIGHT IN LIQUID MIXTURES.

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## 1. *Introduction.*

As is well known, there are many substances, *e.g*, phenol and water, which in the liquid state dissolve each other completely and form a single phase above a certain temperature, but below it are only partially soluble and divide into two co-existent phases. Such mixtures exhibit a marked opalescence or turbidity at temperatures slightly higher than that at which they separate into two layers. Smoluchowski * put forward a thermodynamic explanation of this phenomenon as due to the spontaneous local fluctuations of concentration which occur in the mixture and cause optical inhomogeneity. The problem was further handled by Einstein †, who made certain simplifying assumptions, namely that the liquids are incompressible, that their specific volumes are negligibly small in comparison with those of the saturated vapours emitted by them, and that the latter can be treated as ideal gases, and on this basis derived a formula for the opalescence of the mixture in terms of experimentally determinable magnitudes, that is, the variation of its refractive index and of the partial vapour-pressures of its components with alteration of concentration. The simplifications referred to, however, considerably restrict the validity of the investigation which, in fact, can be regarded as strictly applicable only over a small range of temperature above that at which the mixture separates into two phases. For such a restricted range, the correctness of Einstein's formula has been experimentally established by the investigations of Fürth ‡ and of Zernike §. Actually, however, by using carefully purified liquids freed from dust by repeated distillation *in vacuo*, the opalescence in mixtures may be studied over any desired range of temperature and not merely in the immediate vicinity of the critical solution point, and very remarkable and interesting changes in

* *Annalen der Physik*, xxv, p. 219 (1908).
† *Annalen der Physik*, xxxiii, p. 1295 (1910).
‡ *Wiener Sitzungsberichte*, p. 577, 1915.
§ Thése, Amsterdam, 1915.

the intensity of the scattered light and the state of its polarization are observed. These phenomena are also noticeable in mixtures of liquids which are completely soluble in each other at the ordinary temperature. It is found that Einstein's approximate investigation is not adequate to explain the observed facts in these cases and that a stricter investigation is called for. It is proposed in this paper to show how by a modification of the procedure adopted by Einstein, a *perfectly rigorous* expression for the light scattering can be derived in terms of experimentally determinable quantities. A comparison is also made between the results of the modified theory and those observed in experiment. Specially noteworthy are the effects arising from *molecular anisotropy* which, of course, are not contemplated at all in Einstein's theory. These are discussed in detail in the course of the paper.

## 2. *Thermodynamical Theory: Application of Boltzmann's Principle.*

In order to deal with the problem under consideration, Einstein assumed that the refractive index of the mixture is a function of a single variable $k$ which expresses the concentration of the mixture, that is the ratio of the mass of the second component present to that of the first component. This is not, however, correct. We have in reality to deal with *two* independent variables, namely, the densities of both components, and the local fluctuations of refractive index are determined by variations of both of these quantities. One way of determining the accidental deviations of density in a mixture is by applying the principles of statistical mechanics. This has been attempted by Ornstein *. In order, however, to express the results in terms of physically measurable quantities, it is simpler to use a purely thermodynamical treatment based upon Boltzmann's well-known relation between entropy and probability. In order to make use of this principle, we have to find the change of entropy resulting from small increases $\Delta m_1$ and $\Delta m_2$ in the masses, $m_1$ and $m_2$ of the components actually present in unit volume of the mixture. The probability of such deviations occurring spontaneously and their mean value may then be evaluated. In order to find the change of entropy involved we have to imagine the masses $\Delta m_1$ and $\Delta m_2$ introduced into unit volume of the mixture isothermally and by reversible process. The following thermodynamical operation, which is a modification of that used by Einstein, enables this to be done.

Consider unit volume of the mixture enclosed in a cylinder fitted with a frictionless piston by which the hydrostatic pressure can be varied The base of the cylinder has two openings, which may be either closed at will or fitted with membranes permeable respectively to the vapour of the first and second components only. A second and much larger reservoir similarly fitted with a piston and semi-permeable openings is

* Proc. Roy. Soc. Amsterdam, xv, p. 54 (1912).

assumed to be filled with the liquid mixture, this being maintained at the same temperature and at a hydrostatic pressure equal to the total vapour pressure $\phi$ of the mixture. The following isothermal operations may then be carried out.

*Stage* 1.

By means of auxiliary pumps applied to the semi-permeable openings, small masses $(\Delta m_1)$ and $(\Delta m_2)$ of the two components may be removed in the state of vapour from the reservoir, the volume of which is assumed to be so great that no appreciable alteration in the composition of its contents occurs in consequence of this removal.

If $p_1$ and $p_2$ be respectively the partial pressures of the vapours and $v_1$ and $v_2$ their specific volumes, the work done in the process is

$$-p_1 v_1 \Delta m_1 - p_2 v_2 \Delta m_2 + [s_1 \Delta m_1 + s_2 \Delta m_2]\phi, \quad . \quad . \quad (1)$$

where $s_1$ and $s_2$ represent respectively the shrinkages of the volume of the mixture by removal of unit masses of the two components.

*Stage* 2.

Taking the masses $(\Delta m_1)$ and $(\Delta m_2)$ of the vapours thus separated, force simultaneously a mass $(\Delta m_1)$ of the first component and a mass $(k\Delta m_1)$ of the second component into the cylinder the contents of which are maintained at a constant hydrostatic pressure $\phi$, $k$ being the fraction $m_2/m_1$. It is clear that in this operation the composition of the mixture, and therefore also its vapour-pressure, remain unaltered. The work done in this process in therefore

$$p_1 v_1 \Delta m_1 + p_2 v_2 k \Delta m_1 - [s_1 \Delta m_1 + s_2 k \Delta m_1]\phi. \quad . \quad . \quad (2)$$

*Stage* 3.

Force the remaining portion $(\Delta m_2 - k\Delta m_1)$ of the second component into the cylinder, the hydrostatic pressure in it being maintained at the equilibrium value of its total vapour-pressure at each instant. The work done in this process is

$$v_2(\Delta m_2 - k\Delta m_1)(p_2 + \tfrac{1}{2}\Delta p_2) - s_2(\Delta m_2 - k\Delta m_1)(\phi + \tfrac{1}{2}\Delta\phi), \quad (3)$$

where $(\Delta p_2)$ and $(\Delta\phi)$ represent respectively the changes of the partial vapour-pressure and the total vapour-pressure resulting from the operation.

*Stage* 4.

The volume of the mixture in the smaller cylinder is now greater than at first by $(s_1\Delta m_1 + s_2\Delta m_2)$. The semi-permeable openings are now closed, and the piston enclosing the contents forced in by increasing the hydrostatic pressure till the original volume is restored. The work done in this process is

$$\tfrac{1}{2}\beta\,(\Delta p)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\beta$ is the compressibility of the mixture and $(\Delta p)$ si the increase of hydrostatic pressure in the process.

Adding up (1), (2), (3), and (4) we find the total work done is

$$\tfrac{1}{2}(v_2\Delta p_2 - s_2\Delta\phi)(\Delta m_2 - k\Delta m_1) + \tfrac{1}{2}\beta(\Delta p)^2 \quad . \quad . \quad . \quad (5)$$

The quantity $k$ is a measure of the concentration of the mixture. If it be altered to $k+\Delta k$ as the result of the operations set out above, it is easily seen that $m_1\Delta k = (\Delta m_2 - k\Delta m_1)$.

Hence (5) may be written in the form

$$\tfrac{1}{2}m_1\left(v_2\frac{\partial p_2}{\partial k} - s_2\frac{\partial\phi}{\partial k}\right)(\Delta k)^2 + \tfrac{1}{2}\beta(\Delta p)^2,$$

or, for brevity,

$$\tfrac{1}{2}\alpha(\Delta k)^2 + \tfrac{1}{2}\beta(\Delta p)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The next step is to find the mean value of $(\Delta k)^2$ and $(\Delta p)^2$ in the deviations which occur spontaneously in a volume-element $dv$ of the mixture. We may for this purpose use Boltzmann's principle in the form in which it has been expressed by Einstein,

$$dW = Ce^{-\frac{NE}{RT}}\,d\lambda_1 d\lambda_2 \ldots d\lambda_n, \quad . \quad . \quad . \quad . \quad (7)$$

where $\lambda_1, \lambda_2 \ldots . \lambda_n$ are suitably chosen variables which determine the observable condition of the system and $dW$ is the probability that the magnitudes $\lambda_1$, $\lambda_2$, etc., lie between $\lambda_1$ and $\lambda_1 + d\lambda_1$ $\lambda_2$ and $\lambda_2 + d\lambda_2$, etc., R, T, and N have the same significance as in kinetic theory. C is a constant and E is the work necessary to bring the system into the state under consideration from that of thermodynamical equilibrium. If $\lambda_1$, $\lambda_2$ . . . . are assumed to be zero in the state of equilibrium and E can be expressed in the form

$$E = \tfrac{1}{2}a_1\lambda_1^2 + \tfrac{1}{2}a_2\lambda_2^2 + \ldots . + \tfrac{1}{2}a_n\lambda_n^2, \quad . \quad . \quad . \quad (8)$$

then (7) assumes the familiar form of the Gaussian error-law and it may easily be shown by integration that

$$\left.\begin{array}{l}\overline{\lambda_1^2} = RT/Na_1,\ \overline{\lambda_2^2} = RT/Na_2, \text{ etc.,} \\ \overline{\lambda_1\lambda_2} = \overline{\lambda_2\lambda_3} \ldots . = 0,\end{array}\right\} \quad . \quad . \quad . \quad (9)$$

where the bars indicate the *mean value* of the quantities written under them.

Comparing (6) and (8), we find from (9) that for an elementary volume $dv$ of the mixture

$$\left.\begin{array}{r}\overline{(\Delta k)^2} = \dfrac{RT}{N}\dfrac{1}{\alpha dv}, \\ \overline{(\Delta p)^2} = \dfrac{RT}{N}\dfrac{1}{\beta dv}, \\ \text{and } \overline{\Delta k}\,\overline{\Delta p} = 0.\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Writing $\epsilon = \mu^2$ where $\mu$ is the refractive index of the mixture

$$\Delta\epsilon = \frac{\partial \epsilon}{\partial k}.\Delta k + \frac{\partial \epsilon}{\partial p}\Delta p,$$

and from (10), it follows at once that

$$(\overline{\Delta\epsilon})^2 = \frac{\mathrm{RT}}{\mathrm{N}dv}\left[\left(\frac{\partial \epsilon}{\partial k}\right)^2\Big/\alpha + \left(\frac{\partial \epsilon}{\partial p}\right)^2\Big/\beta\right]. \quad . \quad . \quad (11)$$

### 3. *Intensity of the Scattered Light: Comparison with Einstein's formula.*

From (11), the intensity of the opalescence radiation can be easily calculated. Using a relation given by the late Lord Rayleigh *, we find that in a direction at right angles to the incident beam (assumed to be unpolarized and of unit intensity), the intensity of the scattered light is

$$\mathrm{I} = \Sigma \frac{\pi^2 (dv)^2 (\overline{\Delta\epsilon})^2}{2\lambda^4}\Big/r^2.$$

where $\lambda$ is the wave-length and $r$ is the distance of the volume-element from the point of observation. Substituting for $(\Delta\epsilon)^2$ from (11), and integrating over the whole volume of the fluid, say $\Psi$,

$$\mathrm{I} = \frac{\Psi}{r^2}\cdot\frac{\pi^2\mathrm{RT}}{2\mathrm{N}\lambda^4}\left[\left(\frac{\partial \epsilon}{\partial k}\right)^2\Big/m_1\left(v_2\frac{\partial p_2}{\partial k} - s_2\frac{\partial \phi}{\partial k}\right)\right.$$

$$\left. + \beta\rho^2\left(\frac{\partial \epsilon}{\partial \rho}\right)^2\right], \quad . \quad . \quad (12)$$

where $\rho$ is the density of the mixture.

The principal difference between Einstein's expression for the light-scattering in liquid mixtures and that given here is that the former does not include the term proportional to the compressibility of the mixture which appears in (12). This term expresses the light-scattering due to the local thermal *fluctuations of density* in the mixture considered as a single substance. Using Lorentz's relation $(\epsilon - 1)/(\epsilon + 2) = \text{const.}\ \rho$, the second term in (12) may be developed and written in the form

$$\frac{\pi^2\,\mathrm{RT}\beta}{18\,\mathrm{N}\lambda^4}(\mu^2 - 1)^2(\mu^2 + 2)^2\frac{\Psi}{r^2}. \quad . \quad . \quad (13)$$

The first term in (12) which represents the light-scattering due to the local *fluctuations of concentration* in the mixture may be simplified if we neglect $s_2\,\frac{\partial \phi}{\partial k}$ in comparison with $v_2\,\frac{\partial p_2}{\partial k}$ and assume, further,

* Scientific Papers, vol. i, p. 526.

that the saturated vapour obeys the gas laws, in which case it may be written as

$$\frac{M_2}{2N\lambda^4} \cdot \frac{\frac{1}{m_1}(\partial\epsilon/\partial k)^2}{\partial \log p_2/\partial k} \cdot \frac{\Psi}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where $M_2$ is the molecular weight of the second component in the gaseous phase. (14) is Einstein's approximate result. The simplifications here made are only permissible when the vapour-pressure is not large.

The relative importance of the two effects, viz., the light-scattering due to fluctuations of density and concentration respectively, which contribute to its total observed intensity depends on the circumstances of the particular case. The first effect depends on the refractive index and compressibility of the mixture, and second on the variations of refractive index and of the partial vapour-pressures produced by a change in the composition of the mixture. In the immediate neighbourhood of the critical solution temperature, the partial vapour-pressures alter very little with the composition of the mixture, and the concentration-scattering becomes very great. On the other hand, at temperatures far removed from the critical solution point or in the cases in which the components are ordinarily completely miscible, the partial vapour-pressures change rapidly with concentration, the concentration scattering becomes less, and if the refractive indices of the components do not differ much, it may even become unimportant in comparison with the density scattering. The relative proportion of the two components in the mixture is also of importance. It is evident that when either of the components forms a vanishingly small proportion of the mixture, the concentration-scattering would disappear and the observed opalescence would be due entirely to the density-scattering in the remaining component. The composition of the liquid would also influence the density-scattering, since the refractive index and compressibility of the mixture are both functions of it.

### 4. *Effect of Molecular Anisotropy.*

The theory so far discussed rests on a purely thermodynamical basis and leads to the result that the light scattered in a direction transverse to the primary beam should be completely polarized. If we had proceeded on the basis of a molecular theory we should have obtained a precisely identical result, provided the molecules could be treated as isotropic or spherical scattering particles exerting forces on each other. Actually, however, this is far from being the case. Even in the case of gases, the transversely scattered light is known to be imperfectly polarized, and in liquids at ordinary temperatures this imperfectness of polarization of the scattered light is found to be much more strikingly evident. Taking this into account, we may, in considering the case of liquid mixtures, divide the total observed light-scattering in a direction

transverse to the primary beam into three parts, which are assumed to be superposed on each other. A part $\Omega_1$ arises from density fluctuations. A part $\Omega_2$ arises from the concentration fluctuations. Both of these consist of polarized light, and their magnitudes are given by the thermodynamic theory already considered. Another part arises from the varying orientations of the anisotropic molecules, and this consists in great measure of unpolarized light. Denoting by $r$ the ratio of intensity of the weak to the stong component of polarization in the transversely scattered light, we may write.

$$r = \frac{2\Omega_4}{\Omega_1 + \Omega_2 + \Omega_3 + 2\Omega_4}, \qquad (15)$$

where $\Omega_3 + 4\Omega_4$ is the total intensity of the orientation-scattering of which a part $\Omega_3$ consists of plane polarized light and the remaining portion, $4\Omega_4$, consists of unpolarized light, and is therefore equally divided between the two perpendicular directions of vibration. For all practical purposes $\Omega_3$* is negligible, and it remains to determine the magnitude of $\Omega_4$.

If we assume that the molecules in a liquid have their *orientations* entirely at random (though their *positions* are *not*), it is readily seen that the unpolarized part of the orientation-scattering would be simply proportional to the number of molecules $n_1$ and $n_2$ of each kind present in unit volume, and we may write.

$$\Omega_4 = n_1 \chi_1 + n_2 \chi_2, \qquad (16)$$

where $\chi_1$, $\chi_2$ are constants characteristic of each kind of molecule. The magnitude of $\chi_1$ and $\chi_2$ may be determined from (15) and (16) when the values of $r$ corresponding to the case in which the liquid contains only one component or the other are known, and the values of $r$ and $\Omega_4$ for any given composition of the mixture may then readily be calculated. The assumption that the orientation-scattering is simply proportional to the number of molecules per unit of volume is shown to be justified by the fact that in a number of cases it enables the value of $r$ to be successfully predicted for a single substance in the state of liquid when the corresponding value of $r$ for the same substance in the state of vapour is known.

It is evident from (15) that when $\Omega_1$ or $\Omega_2$ is very large, $r$ will be very small. In other words, when either the density scattering or the concentration-scattering is very large, the transversely-scattered light is almost completely polarized. The latter condition arises when the observations are made in the immediate vicinity of the

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* In the case of gases obeying Boyle's law, only 1/13 of the orientation-scattering consists of polarized light, as has been shown by Born. In the case of liquids under ordinary conditions, it is probably much smaller on account of the partial correlation of phase of the effects of contiguous molecules.

critical solution temperature. The former condition arises at the plait-point temperature of the mixture, *i.e.*, at a temperature which corresponds to the ordinary critical state for a simple fluid. In either of these cases, the orientation-scattering is a negligible part of the whole observed scattering.

### 5. *Comparison of Theory and Experiment.*

The theoretical results deduced above agree in their general features with experiment. The scattering of light by mixtures of phenol and water of varying concentrations has been studied in the authors' laboratory by Mr. V. S. Tamma for a range of 30° C. above its critical solution temperature (68° C.). The scattering is exceedingly large in the immediate neighbourhood of the critical solution point, and as the temperature is raised its intensity diminishes, but over the whole range the scattering remains much higher than that of the pure liquids taken together or separately. As is indicated by theory, the polarization of the light scattered in the mixture is far more complete than in pure phenol, which shows a large admixture of unpolarized light. Very near the critical solution temperature, the polarization is practically complete. But as the temperature is raised, it becomes less and less perfect.

Experiments have also been made on mixtures of ethyl alcohol and water. As the percentage of alcohol is increased, the scattering increases to a maximum, then comes down to a minimum and again increases. The extra scattering is largest for a mixture containing about 20 per cent. of alcohol. The case of this mixture is particularly complicated, inasmuch as both its compressibility and refractivity are anomalous. At 20° C., the compressibility is a minimum when the percentage by weight of alcohol is nearly 20. The refractivity of the mixture increases as the alcohol-content is increased, and reaches a maximum when there is about 80 per cent. by weight of alcohol, after which it again diminishes.

The following table gives the density-scattering calculated for different compositions in terms of that of water as a unit :—

| Percentage of alcohol by weight. | Compressibility at 20° $\times 10^6$. | Refractive index at 20° C. | Density scattering. |
|---|---|---|---|
| 0 | 49 | 1·3375 | 1·00 |
| 10 | 42 | 1·3436 | 0·94 |
| 20 | 40 | 1·3500 | 0·94 |
| 40 | 47 | 1·3600 | 1·20 |
| 60 | 62·5 | 1·3670 | 1·68 |
| 80 | 81 | 1·3693 | 2·19 |
| 100 | 100 | 1·3674 | 2·72 |

To calculate the concentration-scattering, we require to know the partial vapour-pressures of the components, and curiously enough, the necessary data do not seem to exist for alcohol-water mixtures. Anyhow, the concentration-scattering would vanish at about 80 per cent. by

weight of alcohol, since at that point there is no change of refractivity with concentration, and would be very small over the range 60 to 100 per cent. Since the refractivity of alcohol is not very different from that of water, the effect would not be large at any stage. This agrees with the observed facts.

Measurements of the intensity and polarization of the scattered light in binary mixtures of carbon disulphide and ether, and of benzene and normal hexane have been published by W. H. Martin.* By the use of relation (15), we can calculate the orientation-scattering. Partial vapour-pressure data for the first mixture are available †, and from (14) the concentration-scattering can be calculated. But owing to lack of compressibility data, we cannot calculate the density-scattering. Since, however, this forms only a small fraction of the total scattering in the present case, an error in its estimate would not be of much consequence.

In the attached graph are shown, A the concentration-scattering, B the unpolarized scattering, and C the sum of these two for different concentrations. The values of the total experimental scattering are also plotted in curve D. It will be seen that the curve of orientation-scattering is nearly a straight line, showing, in agreement with (16), that it is proportional to the number of the two kinds of molecules per unit volume. The concentration-scattering was calculated by using (14).

Now

$$\frac{\partial \log p_2}{\partial k} = \frac{1}{p_2}\frac{\partial p_2}{\partial k} = -\frac{x^2}{p_2}\frac{\partial p_2}{\partial x},$$

where $x$ is the mass of the first component (in this case $CS_2$) in unit mass of the mixture. The values of $\frac{\partial p_2}{\partial x}$ were got from the partial vapour-pressure curve of ether. $\frac{\partial \epsilon}{\partial x}$ was calculated from the formula for the refractive index of mixtures

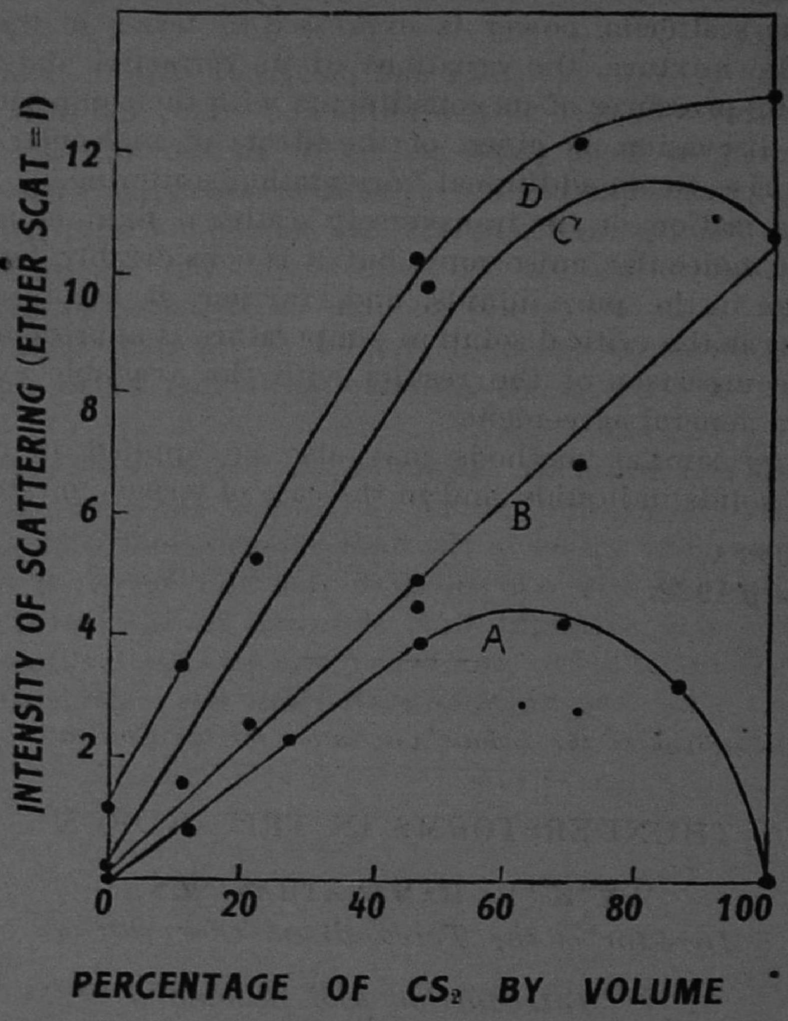
$$\frac{\epsilon-1}{(\epsilon+2)\rho} = \frac{\epsilon_1-1}{(\epsilon_1+2)\rho_1}x + \frac{\epsilon_2-1}{(\epsilon_2+2)\rho_2}(1-x),$$

where $\epsilon_1$, $\rho_1$, and $\epsilon_2$, $\rho_2$ refer to the two components of the mixture.

It will be noticed that the curve C closely follows the experimental intensity-curve. The difference, no doubt, represents the density-scattering, which, however, cannot be calculated theoretically (except separately for the two pure liquids) as the compressibility of the mixture

* Journal of Physical Chemistry, Jan. 1922.
† Guglielmo, *Acc. dei Lincei* (5) 1, i. pp. 242 & 294 (1892).

is not known. For pure ether and pure $CS_2$ the density-scatterings are 0·85 and 2·80, so that if these are added to the orientation-scatterings, the total scattering fits into Martin's experimental curves. To make an




adequate test of the theory, we require to know both the compressibilities and the partial vapour-pressures of pairs of liquids. Data regarding partial vapour-pressures are available for a number of pairs of liquids, and the measurement of compressibilities of mixtures is being undertaken in this laboratory in order to make a complete test of the theory of light-scattering in mixtures.

## *Summary and Conclusion.*

In this paper, the approximate investigation of the scattering of light in liquid mixtures given by Einstein is revised and a perfectly rigorous formula is developed, in which account is taken of the compressibility of the mixture. It is shown that the thermodynamical investigation leads to the result that the light-scattering arises in two distinct ways : (1) due to spontaneous local fluctuations in the composition of the mixture, and (2) due to local fluctuations of its density.

Einstein's approximate investigation ignores the second effect, which becomes very important when the observations are made at temperatures not close to the critical solution point or in the case of liquids which are completely miscible at ordinary temperatures.

(*a*) The scattering power is expressed in terms of the compressibility of the mixture, the variations of its refractive index, and the partial vapour-pressures of its constituents with the composition.

(*b*) A discussion is given of the effects of molecular anisotropy which gives rise to an additional "orientation-scattering." It is shown that the polarization of the transversely scattered light is imperfect as the result of molecular anisotropy, but it is considerably less so in the mixture than in the pure liquids, and, further, it becomes more and more perfect as the critical solution temperature is approached.

(*c*) A comparison of the results with the available experimental data shows a general agreement.

(*d*) Very similar methods may also be applied in the case of solutions of solids in liquids, and in the case of ternary mixtures.

CALCUTTA,
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# THUNDERSTORMS IN TRIVANDRUM

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## *I.—Introduction and Summary.*

Thunderstorms are a regular feature of Trivandrum weather. They present well-marked seasonal and diurnal variations. The maximum activity occurs during the months March to May and in October. In the following paper, an analysis is made of the seasonal variations of thunderstorms in Trivandrum and they are discussed together with the variations of other meteorological elements, humidity, temperature and air movement both at Trivandrum and at Augustia (6,200 ft. above sea level) in the light of Simpson's theory of thunderstorm formation. According to Simpson, whenever there are strong humid, ascending air currents in the atmosphere accompanied by condensation of moisture, splitting of water-drops and separation of electricity occur. The conditions that have been recognized as essential for the formation of strong humid ascending air currents are (1) sufficient moisture in the atmosphere and (2) a vertical temperature-gradient exceeding the adiabatic lapse-rate. So far as these two factors go, they are satisfied at Trivandrum at all the months of the year. The reason why thunderstorms do not occur at all seasons is shown to be connected with the

existence of strong horizontal winds at and above the level of the Western Ghats in the months June to September and November to February, and the comparative absence of such steady air movements during the rest of the year. Strong horizontal winds prevent the formation of strong ascending currents.

## *II.—Statistics of Thunderstorms.*

Observations of thunderstorms in Trivandrum made during the years 1856-1864 by Mr. J. A. Broun have been discussed in the Indian Met. Memoirs, Vol. X, part 1 by Sir J. Eliot. Further records have been kept in the Trivandrum Observatory from 1892 onward, when they were begun by Dr. A. C. Mitchell.

Table I gives the number of days on which thunder was heard in the different months of the years 1902—1914.

Table II gives the number of days on which lightning was seen with or without thunder.

TABLE I.—Number of days on which thunder was heard.

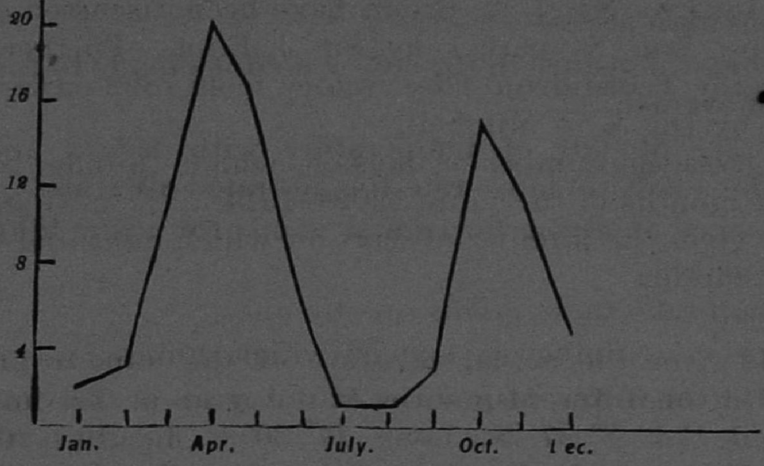
| Year. | Jan. | Feb. | Mar. | Apr. | May. | June. | July. | Aug. | Sep. | Oct. | Nov. | Dec. | TOTAL. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1902 | 3 | 1 | 13 | 28 | 23 | 10 | 0 | 0 | 6 | 16 | 14 | 8 | 122 |
| 1903 | 2 | 2 | 6 | 26 | 17 | 10 | 0 | 0 | 2 | 11 | 8 | 7 | 91 |
| 1904 | 2 | 2 | 9 | 19 | 13 | 8 | 4 | 0 | 0 | 22 | 9 | 1 | 89 |
| 1905 | 0 | 4 | 4 | 23 | 15 | 2 | 0 | 0 | 2 | 10 | 9 | 0 | 69 |
| 1906 | 0 | 5 | 7 | 14 | 19 | 3 | 0 | 3 | 1 | 20 | 13 | 8 | 90 |
| 1907 | 2 | 1 | 17 | 22 | 21 | 5 | 2 | 1 | 14 | 19 | 12 | 7 | 113 |
| 1908 | 7 | 8 | 14 | 17 | 12 | 6 | 1 | 0 | 1 | 8 | 7 | 2 | 83 |
| 1909 | 1 | 7 | 14 | 22 | 11 | 1 | 1 | 2 | 0 | 14 | 14 | 7 | 94 |
| 1910 | 1 | 6 | 13 | 18 | 12 | 5 | 4 | 3 | 1 | 11 | 15 | 0 | 89 |
| 1911 | 0 | 1 | 12 | 6 | 17 | 5 | 1 | 0 | 3 | 15 | 8 | 10 | 78 |
| 1912 | 1 | 4 | 5 | 24 | 22 | 6 | 0 | 0 | 3 | 14 | 10 | 0 | 101 |
| 1913 | 3 | 4 | 7 | 20 | 21 | 4 | 1 | 2 | 2 | 10 | 10 | 6 | 88 |
| 1914 | 2 | 3 | 13 | 19 | 16 | 8 | 1 | 2 | 5 | 14 | 11 | 7 | 101 |
| Average | 2 | 3 | 10 | 20 | 17 | 6 | 1 | 1 | 3 | 15 | 11 | 5 | 93 |

TABLE II.—Number of days on which lightning was seen with or without thunder.

| Year. | Jan. | Feb. | Mar. | Apr. | May. | June. | July. | Aug. | Sep. | Oct. | Nov. | Dec. | TOTAL. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1902 | 3 | 2 | 16 | 29 | 30 | 14 | 0 | 2 | 8 | 22 | 18 | 11 | 155 |
| 1903 | 2 | 4 | 10 | 30 | 22 | 12 | 0 | 0 | 2 | 15 | 15 | 9 | 121 |
| 1904 | 2 | 6 | 14 | 22 | 22 | 9 | 4 | 1 | 2 | 22 | 9 | 4 | 117 |
| 1905 | 0 | 10 | 13 | 26 | 26 | 2 | 0 | 0 | 5 | 11 | 16 | 4 | 113 |
| 1906 | 7 | 3 | 12 | 15 | 20 | 5 | 0 | 7 | 4 | 22 | 13 | 10 | 118 |
| 1907 | 2 | 7 | 26 | 25 | 25 | 8 | 5 | 1 | 5 | 24 | 15 | 7 | 150 |
| 1908 | 9 | 11 | 17 | 20 | 15 | 6 | 2 | 0 | 4 | 10 | 7 | 3 | 104 |
| 1909 | 1 | 10 | 16 | 23 | 18 | 3 | 1 | 2 | 0 | 18 | 19 | 8 | 119 |
| 1910 | 1 | 6 | 14 | 19 | 14 | 11 | 5 | 3 | 1 | 14 | 17 | 0 | 105 |
| 1911 | 2 | 2 | 16 | 10 | 19 | 8 | 1 | 1 | 6 | 15 | 16 | 12 | 108 |
| 1912 | 2 | 7 | 10 | 28 | 28 | 19 | 1 | 3 | 10 | 15 | 16 | 3 | 142 |
| 1913 | 4 | 6 | 6 | 24 | 25 | 8 | 1 | 2 | 8 | 14 | 17 | 7 | 122 |
| 1914 | 3 | 4 | 18 | 22 | 18 | 9 | 1 | 2 | 10 | 21 | 16 | 9 | 133 |
| Average | 3 | 6 | 14 | 23 | 22 | 9 | 2 | 2 | 5 | 17 | 15 | 7 | 124 |

It will be observed that the maximum thunderstorm activity occurs during March to May. There is also a secondary maximum in October. The distribution of thundery weather during the year is shown graphically in Figure 1.

An examination of the records also shows that the thunderstorms begin either to the north or east of Trivandrum, except just previous to the burst of the monsoon or when depressions are travelling close to




Trivandrum (when they may begin in any direction) and that they are most active during the afternoon hours 2 to 5 p.m.

### *III.—Mode of Formation.*

The most satisfactory theory of thunderstorm formation is that due to Dr. G. C. Simpson.[1] He showed that splashing of water drops by air currents produces electrification, positive on the drops and negative in the air. When there is opportunity for a large breaking up of water drops, a large quantity of electrification is produced. In the region of humid ascending atmospheric currents, there would be condensation of moisture due to adiabatic cooling, and if the ascending currents are strong, the condensed drops would not be allowed to fall down but would be carried up until they reach a certain size and thereafter their shape would get so much out of the spherical that they would become unstable and break up into smaller drops. Dr. Lenard has shown that the limiting size of water drops beyond which they cannot grow without breaking up is about 5 millimetres in diameter and the limiting velocity which drops of this size would acquire on free fall is nearly equal to 8 metres per second. Hence, no drops could fall through an ascending current of air with a vertical velocity greater than 8 metres per second. The drops would be carried up, reach a certain size, break up, and again be carried up, grow, and break up. Dr. Simpson showed

[1] Phill. Trans. Roy. Seciety, 209, p, 379, 1909.

that enough electricity could be produced on the drops by such splashing as would be sufficient to account for the electricity carried down by rain.

Accepting this theory, we shall see how the conditions are favourable for the formation of thunderstorms in the months of March, April and May and in October and November, and how they are unfavourable during the other months.

The conditions favouring strong ascending currents accompanied by large condensation are :—

1. Enough moisture in the lower air for clouds to form as a result of upward movement ;

2. A rate of fall of temperature with height approaching or exceeding the adiabatic lapse rate for saturated air ; and

3. Absence of strong horizontal winds for a few kilometres above the earth's surface.

I. We shall take these points one by one.

Table III gives the actual pressure of the vapour present in the atmosphere in the different months of the year at Trivandrum and at Augustia peak (Lat. 8° 37′ N., Long. 77° 30′ E., height 6,200 feet above sea level and distant 22 miles from Trivandrum, a high solitary peak in the Western Ghats where an Observatory was maintained by the Government of Travancore during the years 1856—58 and in 1864 under the direction of Mr. J. A. Broun for taking magnetic and meteorological observations).

They are taken from the Indian Met. Memoirs, Vol. X, parts I and II and are based on 24 hourly observations of the wet and dry bulb thermometer during the years 1856—64 at Trivandrum and 1856—58 at Augustia :

| Month. | TRIVANDRUM. | Humidity. % | AUGUSTIA (height 6,200 feet). | Humidity. % |
|---|---|---|---|---|
| | Mean vapour pressure in inches of mercury. | | Mean vapour pressure in inches of mercury. | |
| January ... ... ... | 0·69 | 74 | 0·39 | 93 |
| February ... ... ... | 0·68 | 71 | 0·38 | 83 |
| March ... ... ... | 0·78 | 75 | 0·45 | 89 |
| April ... ... ... | 0·83 | 77 | 0·50 | 90 |
| May ... ... ... | 0·87 | 82 | 0·49 | 97 |
| June ... ... ... | 0·82 | 86 | 0·49 | 98 |
| July ... ... ... | 0·79 | 86 | 0·48 | 99 |
| August ... ... ... | 5·79 | 86 | 0·47 | 97 |
| September ... ... | 0·77 | 83 | 0·46 | 97 |
| October ... ... ... | 0·79 | 85 | 0·46 | 97 |
| November ... ... ... | 0·77 | 83 | 0·44 | 97 |
| December ... ... ... | 0·68 | 76 | 0·39 | 94 |

So far as moisture is concerned, there is plenty of it in all seasons of the year. Indeed, it is doubtful whether there are many other places on earth where there is so much of moisture at all seasons of the year.

II. It is not possible to get an accurate idea of the lapse rate of temperature at Trivandrum without observations with sounding balloons. We can, however, get much useful information from a consideration of the mean temperatures at Trivandrum and Augustia during the different months of the year.

Table IV gives the mean temperatures at Trivandrum and Augustia based on 24 hourly observations; 1856–64 at Trivandrum, and 1856–58 at Augustia.

| Month. | Mean temperature at Trivandrum in °C. | Mean temperature at Augustia in °C. | Difference in °C. |
|---|---|---|---|
| January ... ... ... ... | 24·6 | 12·0 | 12·6 |
| February... ... ... ... | 25·6 | 13·5 | 12·1 |
| March ... ... ... ... | 26·9 | 15·3 | 11·5 |
| April ... ... ... ... | 27·0 | 16·4 | 10·6 |
| May ... ... ... ... | 26·7 | 15·2 | 11·5 |
| June ... ... ... ... | 25·3 | 14·8 | 10·5 |
| July ... ... ... ... | 24·8 | 14·3 | 10·5 |
| August ... ... ... ... | 24·8 | 14·2 | 10·6 |
| September ... ... ... | 25·0 | 14·0 | 11·0 |
| October... ... ... ... | 25·0 | 14·0 | 11·0 |
| November ... ... ... | 25·0 | 13·6 | 11·4 |
| December ... ... ... | 24·7 | 12·2 | 12·5 |

The minimum difference occurs during the months of June and July and even in those months, the lapse rate is 0·56° C per 100 metres (6,200 ft. = 1,890 metres) a quantity far exceeding the adiabatic lapse rate for saturated air. According to Hann, the temperature gradient for 100 metres for saturated air at 25° C under conditions of dynamical equilibrium to a height of 2,000 metres from sea level is 0·43° C per 100 metres (Handbuch der Meteorologie, page 182). We have no data as regards temperatures higher up. So far, then, as the first two conditions for ascensional movement are concerned, they are satisfied in all parts of the year. The answer to the question why thunderstorms do not occur in all months of the year, will be clear when we have discussed the third condition.

### *IV.—Character of the air movement in Trivandrum.*

The character of the air movement in Trivandrum is affected to a great extent by the close neighbourhood of the Western Ghats. For about 20 miles to the east of Trivandrum, the country is undulating with hills and hollows, and beyond it, rises the Western Ghats to an average height of 5,000 ft. During the months June to September, when the S.W. monsoon is in full swing, there is a strong steady wind from about N. 60° W. with little diurnal variation. During the months

November to April, the air movement consists of land and sea-breezes. The N.E. winds, that obtain during this period in the south of the Peninsula to the east of the Ghats, do not penetrate into Trivandrum, sheltered as it is, by the protecting effect of the Ghats. The months May and October are months of transition.

Since the air movement at Trivandrum is largely affected by the proximity of the high Western Ghats, it is more useful to consider the air movement at a higher level where the winds would be less hampered by geographical peculiarities. For this purpose, we shall consider the air movement at Augustia. In his discussion of Augustia meteorological observations, Sir J. Elliot summarizes the general character of the air movement thus :—

"The air movement at Augustia differs essentially in many respects from that prevailing at Trivandrum. The peak is the highest point of the South Travancore Hills.

In the months of December, January and February, when steady and moderate strong N.E. winds obtain in the south-west of the Bay and are continued as E.N.E. winds across the districts of Tinnevelly and Madura and when light local land and sea breezes obtain in the Travancore Coast districts and the neighbouring sea area, the air movement at Augustia is determined by (and is a continuation of) the massive atmospheric current from the N.E. over the Bay which is strongest in the S.E. of the Bay and Southern India. In this season, 5% of the wind observations are of Calms, 64% of the winds are from East and 21% from N.E. and only 10% from other directions. The air movement is hence remarkably steady and is on the mean of all the data, from E.N.E., or more exactly, N. 80° E.

"Similar conditions obtain during the third period (June to Sep.). The air movement at Augustia is then determined by the S.W. monsoon air current over the Arabian Sea. During this period, in the years 1856–58, about 4% of the observations were of Calms, 21% were winds from N.W. and 72% from W. and hence only 3% from the remaining six-points. Winds are hence even steadier in this season than in the first season of the year. The mean wind direction is W.N.W.

"The air movement during the remaining five months of the year is essentially of a transitional character. During the second period comprising the months of March, April and May the mean winds in South Madras shift in direction from East in March and April to West in May, in which month they are practically indentical in direction with the mean winds in June. The mean direction of the winds at Augustia during this period shift *pari passu* with the change of direction of the air movement in Southern India and the resultant is almost nil.

"The conditions in the fourth period including the months October and November are similar to those of the second period except that the transition or charge is inverse to that of the second period.

"The number of Calms reported is large; 16% of the wind observations received during this period in 1856–58 were of Calms, so that they were almost as numerous as during the first transitional period March to May. It is also noteworthy that Calms are more numerous in this, as in the second season, during the day than during the night and are most frequent from 11 A.M. to 4 P.M."

*Summary of weather conditions at Augustia.*

| | | |
|---|---|---|
| December, January and February | Calms | 5% |
| | East | 64% |
| | N.E. | 21% |
| | Other directions | 10% |
| March, April and May ... ... ... | Calms | 19% |
| | East | 25% |
| | S.W. | 33% |
| | Other directions | 23% |
| June to September ... ... ... | Calms | 4% |
| | West | 72% |
| | N.W. | 21% |
| | Other directions | 3% |
| October to November ... ... ... | Calms | 16% |
| | West | 25% |
| | East | 32% |
| | Other directions | 27% |

It will be noticed that the time of maximum thunderstorm activity coincides with the time of minimum horizontal air movement at Augustia. *Absence of strong horizontal winds in the higher layers is a* sine que non *of strong ascending currents favourable to thunderstorm development.*

"During the months of March and April, when the general gradient is undefined and is too weak to exercise any control over the air movement, ascending currents begin to rise with the heat of the sun and form detached cumulus heads. These cumuli grow and with the setting in of a light humid breeze from the sea in the afternoon, they grow into large masses often crowned with false cirrus, especially to the north-east of Trivandrum where the land rise is the most marked. By about 3 P.M. the whole sky is clouded and occasional crashes of thunder are heard. This continues for varying intervals of time and is often accompanied by rain. Ordinarily, the sky clears by about 6 P. M. and a clear night follows. As the season advances, however, the thunderstorm continues at night. The general character of the weather is very similar in October.

These considerations should apply to other places where thunderstorms are seasonal. All along the west coast of India and in Ceylon, the setting in of the monsoon is preceded by a period of thunderstorm activity.